

*Supporting Information for
Palladium-Catalyzed Enantioselective Decarboxylative Allylic Alkylation of
Protected Benzoin-Derived Enol Carbonates.*

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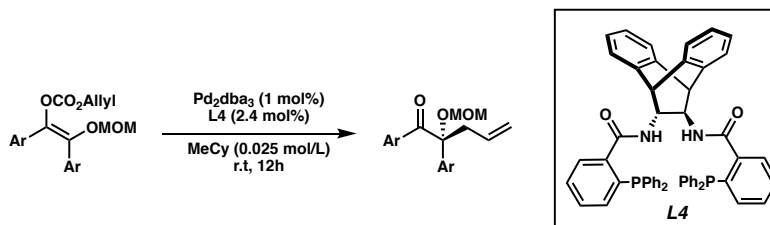
Materials and Methods

Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon.¹ Reaction progress was monitored by thin-layer chromatography (TLC) or Agilent 1290 UHPLC-MS. TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, *p*-anisaldehyde, or KMnO₄ staining. Silicycle SiliaFlash® P60 Academic Silica gel (particle size 40–63 nm) was used for flash chromatography. ¹H NMR spectra were recorded on Varian Inova 500 MHz and Bruker 400 MHz spectrometers and are reported relative to residual CHCl₃ (δ 7.26 ppm). ¹³C NMR spectra were recorded on a Varian Inova 500 MHz spectrometer (125 MHz) and Bruker 400 MHz spectrometers (100 MHz) and are reported relative to CHCl₃ (δ 77.16 ppm). Data for ¹H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septuplet, m = multiplet, br s = broad singlet, br d = broad doublet. Data for ¹³C NMR are reported in terms of chemical shifts (δ ppm). IR spectra were obtained by use of a Perkin Elmer Spectrum BXII spectrometer or Nicolet 6700 FTIR spectrometer using thin films deposited on NaCl plates and reported in frequency of absorption (cm⁻¹). Optical rotations were measured with a Jasco P-2000 polarimeter operating on the sodium D-line (589 nm), using a 100 mm path-length cell. Analytical SFC was performed with a Mettler SFC supercritical CO₂ analytical chromatography system utilizing Chiralpak (AD-H, AS-H or IC) or Chiralcel (OD-H, OJ-H, or OB-H) columns (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd. High resolution mass spectra (HRMS) were obtained from Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI+), atmospheric pressure chemical ionization (APCI+), or mixed ionization mode (MM: ESI-APCI+). Absolute configuration of **4** was determined by X-ray diffraction, and all other products are assigned by analogy.

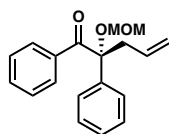
Reagents were purchased from Sigma-Aldrich, Acros Organics, Strem, or Alfa Aesar and used as received unless otherwise stated. Ligand **L4**² and Mom-protected benzoin s were prepared by known methods unless otherwise described below.^{2,3}

List of Abbreviations:

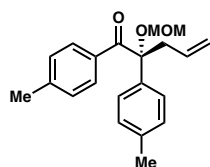
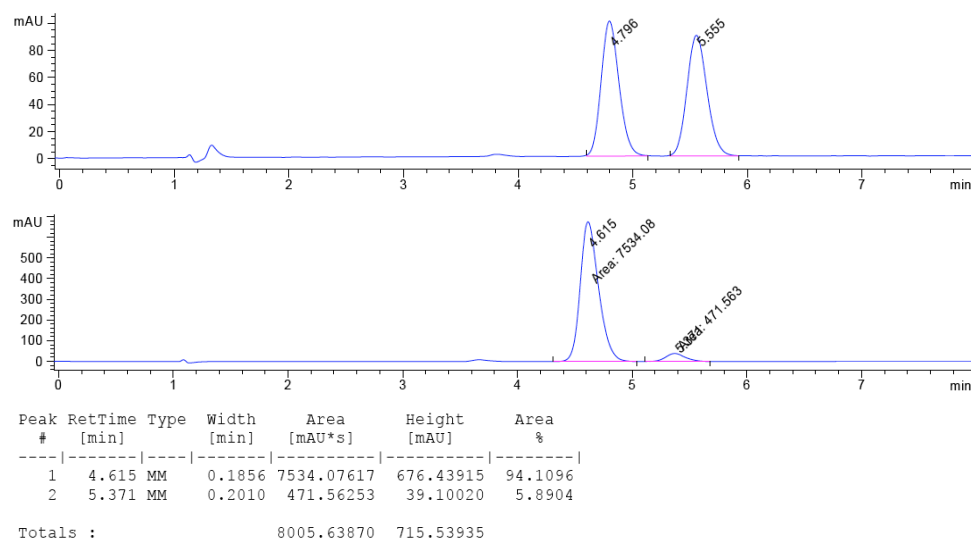
ee – enantiomeric excess, SFC – supercritical fluid chromatography, TLC – thin-layer chromatography, IPA – isopropanol

General Procedure for Pd-Catalyzed Allylic Alkylation Reactions

In a nitrogen-filled glovebox, a solution of $\text{Pd}_2(\text{dba})_3$ (1.8 mg) and **L4** (3.9 mg) in MeCy (4 mL) was stirred for 30 minutes at 25 °C, then the resulting catalyst solution was added to a vial containing allyl enol carbonate substrate (0.2 mmol) in MeCy (4 mL). The vial was sealed with a Teflon-lined cap, removed from the glovebox, and stirred at 25 °C for 12 h. The crude reaction mixture was concentrated then purified by silica gel flash chromatography to provide the desired alkylation product.

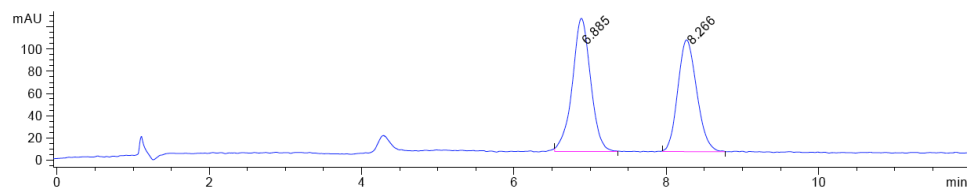
**(S)-2-(methoxymethoxy)-1,2-diphenylpent-4-en-1-one (2a)**

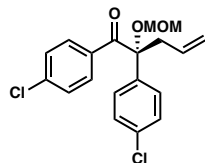
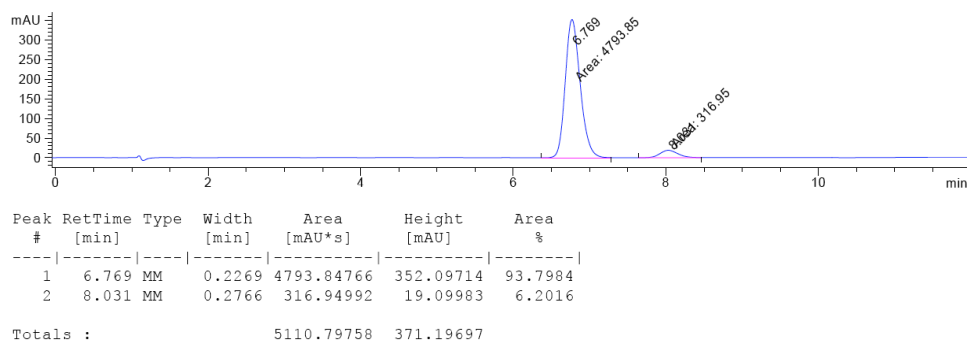
Purified by column chromatography (10% Et_2O in hexanes) to provide a white solid (58.7 mg, 99% yield); 88% ee, $[\alpha]_{\text{D}}^{25} +198.4$ (c 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.84–7.78 (m, 2H), 7.40 – 7.35 (m, 2H), 7.34–7.23 (m, 3H), 7.21–7.15 (m, 3H), 5.46 (dddd, J = 16.9, 10.6, 7.6, 6.3 Hz, 1H), 4.92 – 4.89 (m, 1H), 4.89 – 4.84 (m, 1H), 4.72 (d, J = 6.9 Hz, 1H), 4.66 (d, J = 6.9 Hz, 1H), 3.10 (ddt, J = 15.5, 7.7, 1.2 Hz, 1H), 3.02 (s, 3H), 2.91 (ddt, J = 15.5, 6.4, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.6, 140.7, 135.0, 132.5, 132.4, 130.6, 128.6, 128.0, 127.6, 125.4, 118.5, 93.2, 87.0, 57.1, 40.6; IR (Neat Film, NaCl) 3070, 2926, 1683, 1640, 1597, 1578, 1491, 1446, 1414, 1239, 1182, 1152, 1103, 1078, 1028, 1019, 920, 759, 720, 701, 664 cm^{-1} ; HRMS (MM:ESI-APCI+) m/z calc'd for $\text{C}_{19}\text{H}_{24}\text{NO}_3$ $[\text{M}+\text{NH}_4]^+$: 314.1751, found 314.1753; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_{R} (min): major = 4.62, major = 5.37.



(S)-2-(methoxymethoxy)-1,2-di-*p*-tolylpent-4-en-1-one (2b)

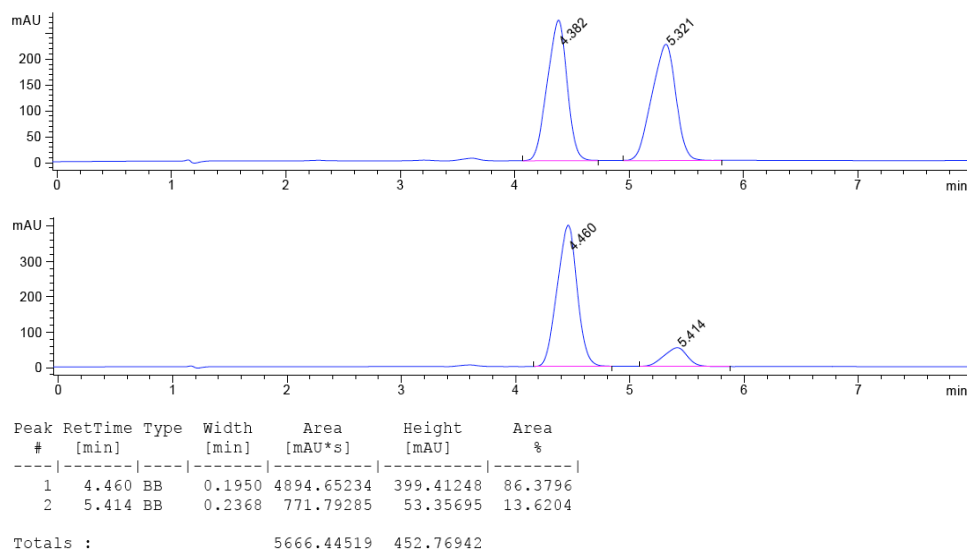
Purified by column chromatography (8% Et₂O in hexanes) to provide a colorless oil (64.3 mg, 99% yield); 88% ee, $[\alpha]_D^{25} +154.6$ (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.79 (m, 2H), 7.36 – 7.28 (m, 2H), 7.18 – 7.10 (m, 2H), 7.10 – 7.00 (m, 2H), 5.63 – 5.47 (m, 1H), 4.99 – 4.91 (m, 2H), 4.76 (d, *J* = 6.8 Hz, 1H), 4.72 (d, *J* = 6.8 Hz, 1H), 3.19 – 3.09 (m, 4H), 2.97 (ddt, *J* = 15.4, 6.3, 1.6 Hz, 1H), 2.31 (s, 3H), 2.29 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 199.3, 143.1, 137.9, 137.1, 132.8, 132.4, 130.8, 129.3, 128.7, 125.3, 118.3, 93.2, 87.0, 57.1, 40.6, 21.7, 21.2; IR (Neat Film, NaCl) 3075, 2922, 2824, 1677, 1640, 1606, 1570, 1511, 1445, 1409, 1242, 1183, 1153, 1101, 1029, 1017, 921, 849, 815, 776, 750 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₂₁H₂₈NO₃ [M+NH₄]⁺: 342.2064, found 342.2062; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, *t_R* (min): major = 6.77, minor = 8.03.

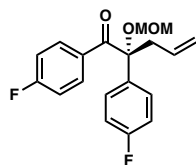




(S)-1,2-bis(4-chlorophenyl)-2-(methoxymethoxy)pent-4-en-1-one (2c)

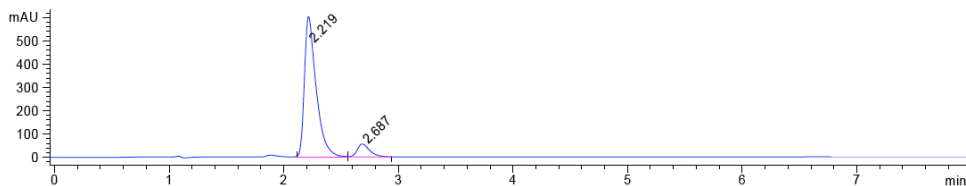
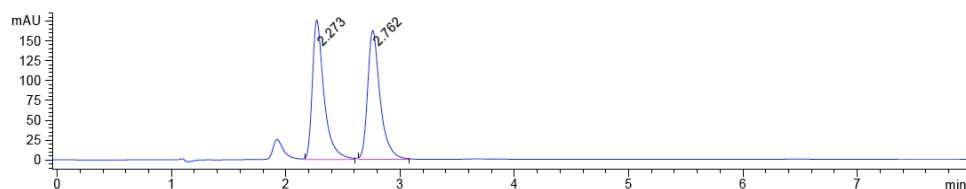
Purified by column chromatography (7% Et₂O in hexanes) to provide a colorless oil (64.7 mg, 89% yield); 73% ee, $[\alpha]_D^{25} +112.9$ (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.78 (m, 2H), 7.34 – 7.26 (m, 4H), 7.26 – 7.19 (m, 2H), 5.46 (dddd, *J* = 17.0, 10.3, 7.4, 6.5 Hz, 1H), 4.99 – 4.87 (m, 2H), 4.80 (d, *J* = 7.0 Hz, 1H), 4.69 (d, *J* = 7.1 Hz, 1H), 3.13 (ddt, *J* = 15.5, 7.5, 1.2 Hz, 1H), 3.08 (s, 3H), 2.88 (ddt, *J* = 15.5, 6.5, 1.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 197.8, 139.1, 139.0, 133.7, 132.9, 132.1, 131.8, 128.9, 128.5, 126.7, 119.1, 93.3, 86.6, 57.3, 40.2; IR (Neat Film, NaCl) 3077, 2926 (br), 1684, 1639, 1588, 1489, 1400, 1244, 1178, 1154, 1092, 1025, 1012, 922, 849, 815, 757, 748 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₁₉H₂₂Cl₂NO₃ [M+NH₄]⁺: 382.0971, found 382.0981; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak IC column, λ = 210 nm, t_R (min): major = 4.46, minor = 5.41.





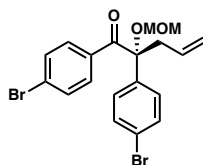
(S)-1,2-bis(4-fluorophenyl)-2-(methoxymethoxy)pent-4-en-1-one (2d)

Purified by column chromatography (10% Et₂O in hexanes) to provide a white solid (65.1 mg, 98% yield); 82% ee, $[\alpha]_D^{25} +155.1$ (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.89 (m, 2H), 7.44 – 7.32 (m, 2H), 7.07 – 6.99 (m, 2H), 6.99 – 6.90 (m, 2H), 5.50 (dddd, *J* = 17.0, 10.4, 7.5, 6.5 Hz, 1H), 5.01 – 4.89 (m, 2H), 4.81 (d, *J* = 7.0 Hz, 1H), 4.72 (d, *J* = 7.0 Hz, 1H), 3.15 (ddt, 15.5, 7.5, 1.3 Hz, 1H), 3.11 (s, 3H), 2.92 (ddt, *J* = 15.5, 6.5, 1.6 Hz, 1H); ¹⁹F NMR (282 MHz, CDCl₃) δ -105.5 (tt, *J* = 8.4, 5.5 Hz), -114.7 (tt, *J* = 8.5, 5.1 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 197.7, 165.1 (d, *J* = 255.0 Hz), 162.2 (d, *J* = 246.7 Hz), 136.4 (d, *J* = 3.2 Hz), 133.4 (d, *J* = 9.1 Hz), 132.0, 131.0 (d, *J* = 3.1 Hz), 127.1 (d, *J* = 8.1 Hz), 118.9, 115.6 (d, *J* = 21.5 Hz), 115.2 (d, *J* = 21.5 Hz), 93.3, 86.6, 57.2, 40.4; IR (Neat Film, NaCl) 3077, 2929 (br), 2848, 2826, 1685, 1640, 1598, 1508, 1445, 1409, 1300, 1237, 1157, 1098, 1024, 1013, 976, 922, 854, 835, 814, 792, 760, 620 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₁₉H₂₂F₂NO₃ [M+NH₄]⁺: 350.1562, found 350.1558; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 2.22, minor = 2.69.



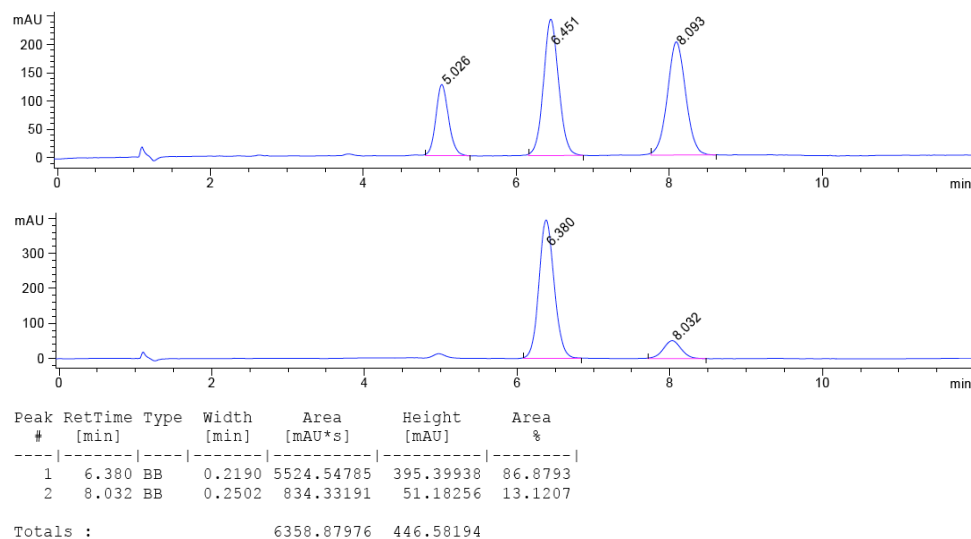
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|--------|---------------|------|-------------|--------------|--------------|---------|
| 1 | 2.219 | BV | 0.1079 | 4291.20605 | 596.60321 | 90.9403 |
| 2 | 2.687 | VB | 0.1180 | 427.49884 | 55.42331 | 9.0597 |

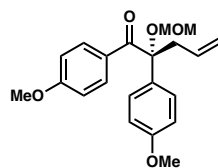
Totals : 4718.70490 652.02652



(S)-1,2-bis(4-bromophenyl)-2-(methoxymethoxy)pent-4-en-1-one (2e)

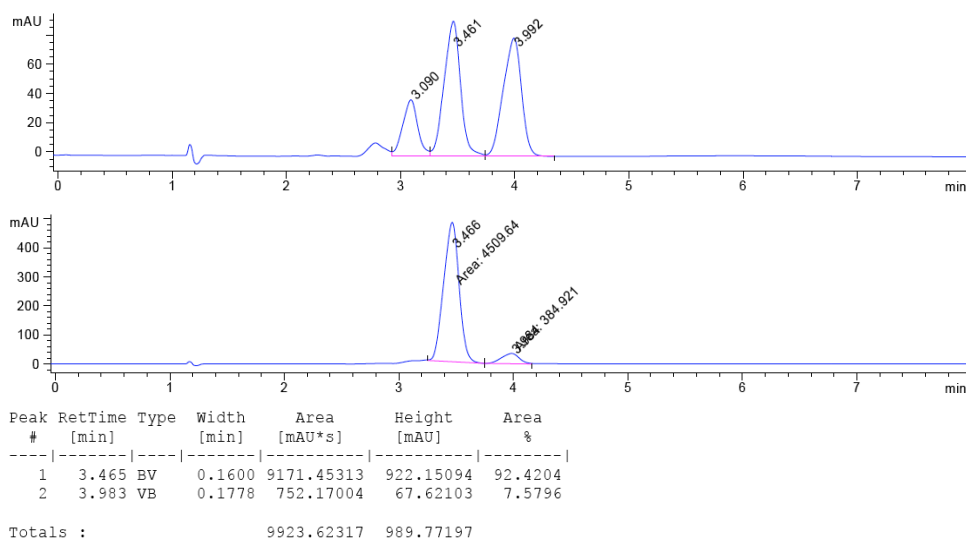
Purified by column chromatography (8% Et₂O in hexanes) to provide a colorless oil (91.6 mg, 99% yield); 74% ee, $[\alpha]_D^{25} +73.9$ (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.79 – 7.71 (m, 2H), 7.51 – 7.37 (m, 4H), 7.31 – 7.22 (m, 2H), 5.47 (dddd, *J* = 17.0, 10.4, 7.5, 6.5 Hz, 1H), 5.03 – 4.89 (m, 2H), 4.81 (d, *J* = 7.0 Hz, 1H), 4.70 (d, *J* = 7.0 Hz, 1H), 3.14 (ddt, *J* = 15.7, 7.5, 1.2 Hz, 1H), 3.09 (s, 3H), 2.88 (ddt, *J* = 15.5, 6.5, 1.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 198.0, 139.6, 133.3, 132.2, 131.9, 131.7, 131.5, 127.9, 127.1, 121.9, 119.1, 93.3, 86.6, 57.3, 40.2; IR (Neat Film, NaCl) 3076, 2928, 1682, 1641, 1583, 1565, 1486, 1445, 1395, 1244, 1178, 1154, 1100, 1072, 1024, 1008, 921, 845, 810, 754, 737 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₁₉H₂₂Br₂NO₃ [M+NH₄]⁺: 469.9961, found 469.9943; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak IC column, λ = 210 nm, *t_R* (min): major = 6.38, minor = 8.03.

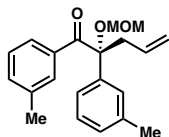




(S)-2-(methoxymethoxy)-1,2-bis(4-methoxyphenyl)pent-4-en-1-one (2f)

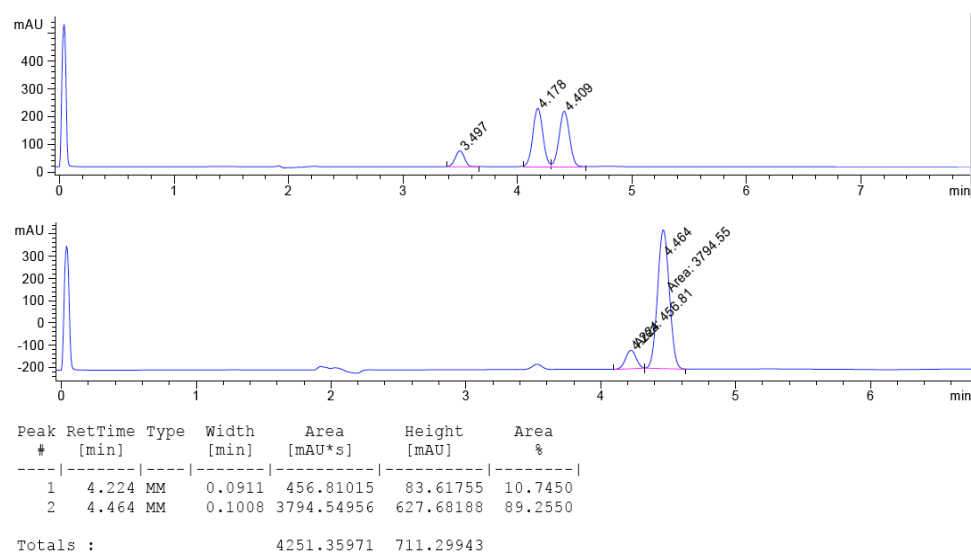
Reaction carried out 48h instead of 12h. Purified by column chromatography (30% Et₂O in hexanes) to provide a colorless oil (71.2 mg, 99% yield); 84% ee, $[\alpha]_D^{25} +129.7$ (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.88 (m, 2H), 7.37 – 7.29 (m, 2H), 6.91 – 6.80 (m, 2H), 6.80 – 6.70 (m, 2H), 5.55 (dddd, *J* = 16.9, 10.6, 7.5, 6.3 Hz, 1H), 5.00 – 4.90 (m, 2H), 4.75 (d, *J* = 6.8 Hz, 1H), 4.72 (d, *J* = 6.8 Hz, 1H), 3.78 (s, 6H), 3.16 (s, 3H), 3.12 (ddt, *J* = 15.4, 7.6, 1.2 Hz, 1H), 2.94 (ddt, *J* = 15.4, 6.3, 1.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 198.2, 162.8, 158.9, 133.1, 133.1, 132.8, 127.8, 126.6, 118.3, 113.9, 113.2, 93.2, 86.8, 57.1, 55.4, 55.3, 40.7; IR (Neat Film, NaCl) 3073, 2935br, 2838, 1671, 1640, 1600, 1574, 1510, 1462, 1443, 1419, 1307, 1249, 1172, 1152, 1101, 1027, 1009, 922, 828, 798, 782, 760, 622 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₂₁H₂₄NaO₅ [M+Na]⁺: 379.1516, found 379.1525; SFC Conditions: 15% IPA, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 3.47, major = 3.98.

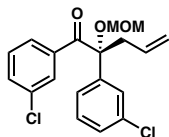




(S)-2-(methoxymethoxy)-1,2-di-*m*-tolylpent-4-en-1-one (2g)

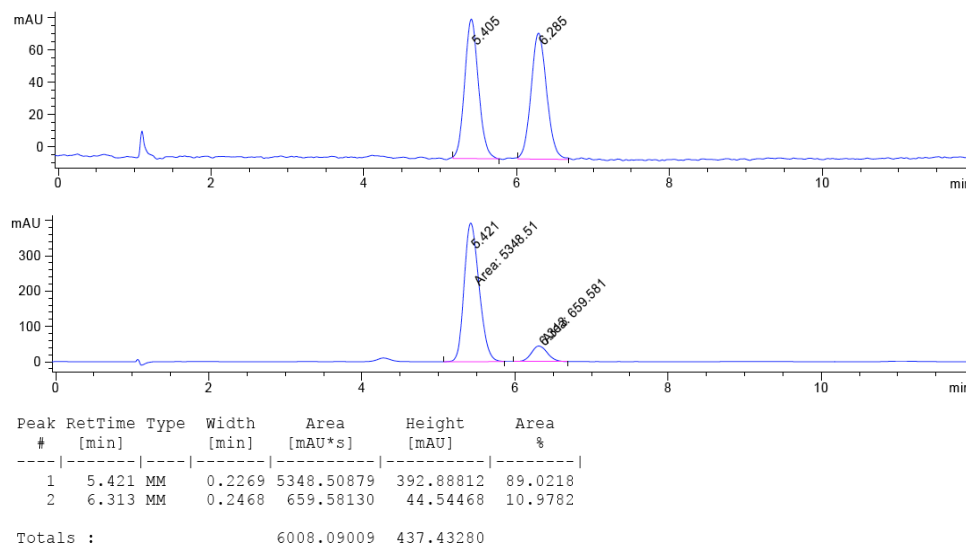
Purified by column chromatography (7% Et₂O in hexanes) to provide a colorless oil (63.4 mg, 97% yield); 79% ee, $[\alpha]_D^{25} +168.0$ (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.74 (td, *J* = 1.8, 1.0 Hz, 1H), 7.65 (dq, *J* = 8.0, 1.2 Hz, 1H), 7.30 – 7.17 (m, 4H), 7.12 (t, *J* = 7.7 Hz, 1H), 7.09 – 7.02 (m, 1H), 5.61 – 5.46 (m, 1H), 4.98 (d, *J* = 1.4 Hz, 1H), 4.97 – 4.92 (m, 1H), 4.76 (d, *J* = 6.8 Hz, 1H), 4.71 (d, *J* = 6.9 Hz, 1H), 3.18 – 3.11 (m, 1H), 3.10 (s, 3H), 2.99 (ddt, *J* = 15.5, 6.2, 1.7 Hz, 1H), 2.33 (s, 3H), 2.29 (d, *J* = 0.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 197.7, 165.1 (d, *J* = 255.0 Hz), 162.2 (d, *J* = 246.7 Hz), 136.4 (d, *J* = 3.2 Hz), 133.4 (d, *J* = 9.1 Hz), 132.0, 131.0 (d, *J* = 3.1 Hz), 127.1 (d, *J* = 8.1 Hz), 118.9, 115.6 (d, *J* = 21.5 Hz), 115.2 (d, *J* = 21.5 Hz), 93.3, 86.6, 57.2, 40.4; IR (Neat Film, NaCl) 3077, 2929 (br), 2848, 2826, 1685, 1640, 1598, 1508, 1445, 1409, 1300, 1237, 1157, 1098, 1024, 1013, 976, 922, 854, 835, 814, 792, 760, 620 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₁₉H₂₂F₂NO₃ [M+NH₄]⁺: 350.1562, found 350.1558; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralcel OD-H column, λ = 210 nm, *t_R* (min): minor = 4.22, major = 4.64.

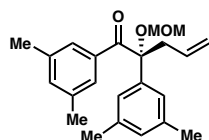




(S)-1,2-bis(3-chlorophenyl)-2-(methoxymethoxy)pent-4-en-1-one (2h)

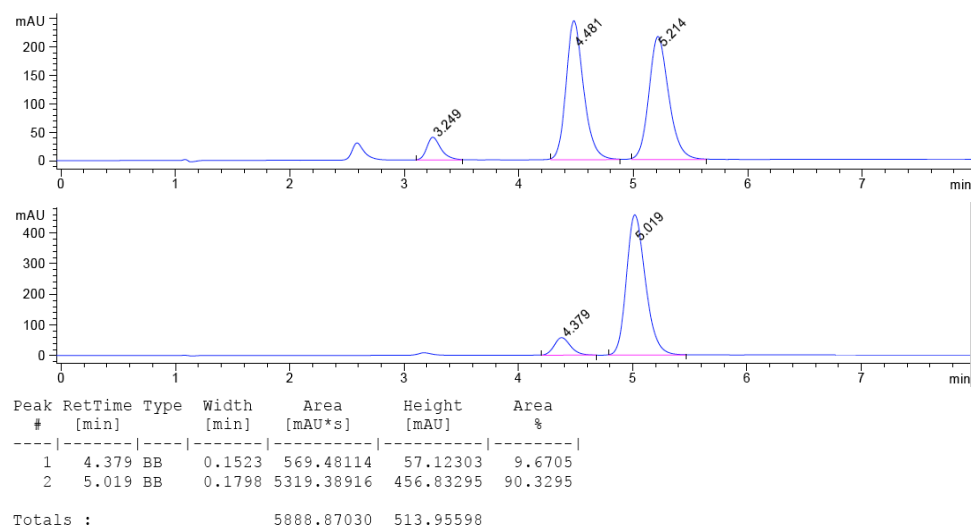
Purified by column chromatography (8% Et₂O in hexanes) to provide a colorless oil (64.9 mg, 78% yield); 78% ee, $[\alpha]_D^{25} +158.0$ (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.90 (ddd, *J* = 2.1, 1.6, 0.4 Hz, 1H), 7.74 (ddd, *J* = 7.9, 1.6, 1.0 Hz, 1H), 7.50 (td, *J* = 1.7, 0.8 Hz, 1H), 7.38 (ddd, *J* = 8.0, 2.2, 1.1 Hz, 1H), 7.27 – 7.19 (m, 4H), 5.48 (dddd, *J* = 16.9, 10.4, 7.5, 6.4 Hz, 1H), 5.05 – 4.91 (m, 2H), 4.84 (d, *J* = 7.1 Hz, 1H), 4.71 (d, *J* = 7.1 Hz, 1H), 3.16 (ddt, *J* = 15.6, 7.5, 1.2 Hz, 1H), 3.09 (s, 3H), 2.92 (ddt, *J* = 15.6, 6.4, 1.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 197.6, 142.5, 136.2, 134.9, 134.4, 132.6, 131.6, 130.5, 130.0, 129.4, 128.8, 128.1, 125.5, 123.5, 119.2, 93.3, 86.6, 57.3, 40.2; IR (Neat Film, NaCl) 3074, 2925, 1686, 1640, 1594, 1570, 1474, 1418, 1278, 1234, 1154, 1079, 1027, 997, 921, 863, 790, 750, 734, 716, 691 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₁₉H₂₂Cl₂NO₃ [M+NH₄]⁺: 382.0971, found 382.0967; SFC Conditions: 3% IPA, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, *t_R* (min): major = 5.42, minor = 6.31.

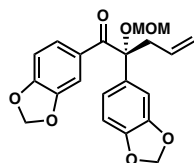




(S)-1,2-bis(3,5-dimethylphenyl)-2-(methoxymethoxy)pent-4-en-1-one (2i)

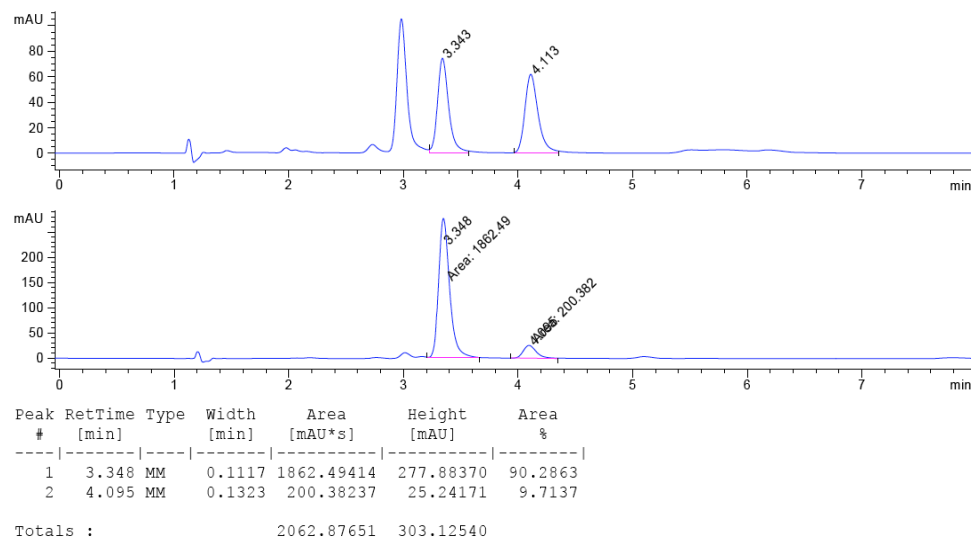
Purified by column chromatography (10% Et₂O in hexanes) to provide a white solid (70.6 mg, 99% yield); 81% ee, $[\alpha]_D^{25} +168.4$ (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.74 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.17 (m, 4H), 7.12 (t, *J* = 7.7 Hz, 1H), 7.06 (d, 1H), 5.61 – 5.46 (m, 1H), 5.01 – 4.92 (m, 2H), 4.76 (d, *J* = 6.8 Hz, 1H), 4.71 (d, *J* = 6.9 Hz, 1H), 3.14 (ddt, *J* = 15.5, 7.7, 1.3 Hz, 1H), 3.10 (s, 3H), 2.99 (ddt, *J* = 15.5, 6.2, 1.7 Hz, 1H), 2.33 (s, 3H), 2.29 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 200.0, 140.6, 138.2, 137.7, 135.1, 133.2, 132.7, 130.9, 128.4, 128.4, 128.1, 127.8, 125.9, 122.5, 118.3, 93.2, 87.1, 57.0, 40.7, 21.8, 21.5; IR (Neat Film, NaCl) 2921 (br), 1680, 1639, 1602, 1585, 1484, 1444, 1258, 1215, 1182, 1150, 1090, 1030, 921, 766, 741, 708 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₂₁H₈NO₃ [M+NH₄]⁺: 325.1798, found 325.1792; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, *t_R* (min): minor = 4.38, major = 5.02.

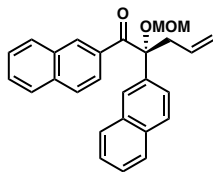




(S)-1,2-bis(benzo[d][1,3]dioxol-5-yl)-2-(methoxymethoxy)pent-4-en-1-one (2j)

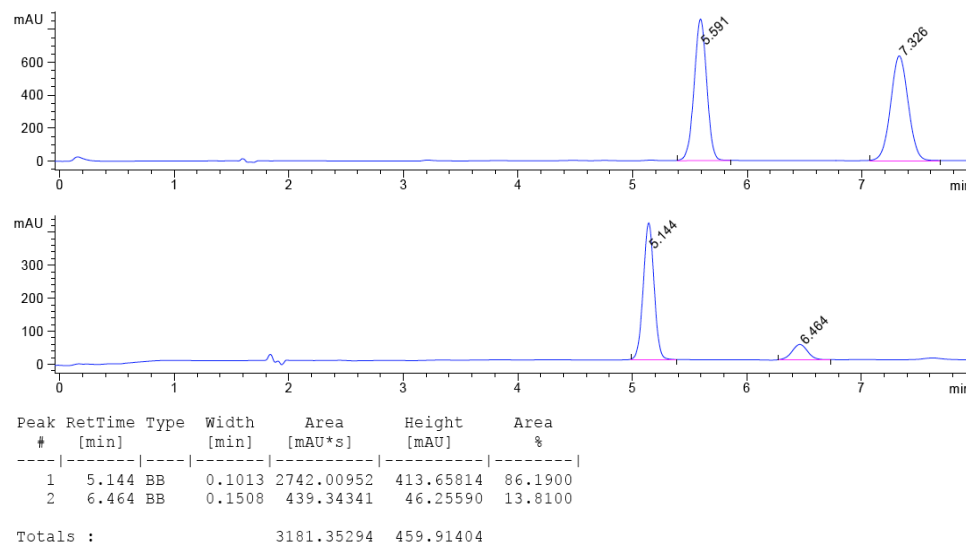
Reaction carried out 48h instead of 12h. Purified by column chromatography (25% Et₂O in hexanes) to provide a colorless oil (56.5 mg, 74% yield); 80% ee, $[\alpha]_D^{25} +104.1$ (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.62 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.45 (d, *J* = 1.7 Hz, 1H), 6.96 (d, *J* = 1.8 Hz, 1H), 6.82 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 6.70 (d, *J* = 8.3 Hz, 1H), 5.99 – 5.92 (m, 4H), 5.54 (dddd, *J* = 16.9, 10.5, 7.5, 6.4 Hz, 1H), 5.02 – 4.92 (m, 2H), 4.75 (d, *J* = 6.8 Hz, 1H), 4.71 (d, *J* = 6.8 Hz, 1H), 3.20 (s, 3H), 3.09 (ddt, *J* = 15.5, 7.5, 1.2 Hz, 1H), 2.90 (ddt, *J* = 15.5, 6.5, 1.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 197.4, 151.1, 148.0, 147.4, 146.9, 135.0, 132.6, 129.2, 127.2, 118.7, 118.4, 110.5, 108.4, 107.7, 106.1, 101.7, 101.3, 93.3, 86.8, 57.2, 40.8; IR (Neat Film, NaCl) 3075, 2898 (br), 2784, 1673, 1640, 1604, 1504, 1487, 1437, 1350, 1254, 1157, 1105, 1039, 934, 814, 793, 756 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₂₁H₂₀NaO₇ [M+Na]⁺: 407.1101, found 407.1105; SFC Conditions: 20% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 254 nm, *t_R* (min): major = 3.35, minor = 4.10.

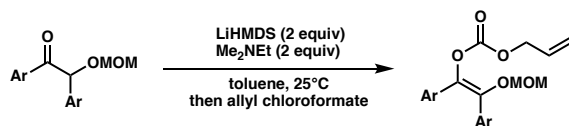




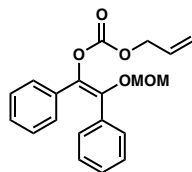
(S)-2-(methoxymethoxy)-1,2-di(naphthalen-2-yl)pent-4-en-1-one (2k)

Purified by column chromatography (12% Et₂O in hexanes) to provide a white amorphous solid (79.2 mg, 97% yield); 72% ee, $[\alpha]_D^{25} +127.4$ (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.53 (s, 1H), 8.06 (s, 1H), 8.00 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.89 – 7.84 (m, 1H), 7.84 – 7.78 (m, 2H), 7.77 – 7.70 (m, 2H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.58 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.51 – 7.45 (m, 3H), 7.41 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 5.59 (dddd, *J* = 16.8, 10.4, 7.6, 6.3 Hz, 1H), 5.02 – 4.93 (m, 2H), 4.91 (d, *J* = 7.0 Hz, 1H), 4.84 (d, *J* = 7.0 Hz, 1H), 3.32 (ddt, *J* = 15.5, 7.6, 1.1 Hz, 1H), 3.15 (ddt, *J* = 15.5, 6.3, 1.6 Hz, 1H), 3.10 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 199.4, 138.4, 135.1, 133.3, 132.8, 132.7, 132.4, 132.3, 132.3, 129.9, 128.5, 128.4, 127.8, 127.7, 127.6, 126.4, 126.4, 126.3, 126.2, 124.5, 123.3, 118.6, 93.4, 87.4, 57.3, 40.6; IR (Neat Film, NaCl) 3059, 2932 (br), 1679, 1640, 1625, 1596, 1507, 1464, 1436, 1353, 1274, 1220, 1190, 1152, 1130, 1099, 1075, 1027, 999, 921, 859, 821, 774, 757 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₂₇H₂₄NaO₃ [M+Na]⁺: 419.1618, found 419.1623; SFC Conditions: 2% IPA, 2.5 mL/min, Chiralcel OJ-H column, λ = 254 nm, *t_R* (min): major = 5.14, minor = 6.46.

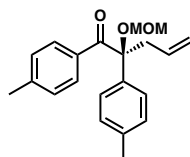


General Procedure for Preparation of Allyl Enol Carbonate Substrates

To a flame-dried flask was added LiHMDS (335 mg, 2 mmol) followed by toluene (3.0 mL) and N,N-dimethylethylamine (0.213 mL) and the resulting mixture stirred at 25 °C for 5 minutes. A solution of ketone (1 mmol) in toluene (2.0 mL) was then added, and the reaction stirred at 25 °C for an additional 30 minutes. The flask was then submerged in a room temperature water bath, and allyl chloroformate (0.217 mL, 2 mmol) was added neat, and the reaction continued until no starting material remained by TLC (typically less than 30 minutes). The crude reaction mixture was diluted with Et₂O and quenched with water. The layers were separated, and the aqueous layer was extracted with Et₂O twice. The combined organic layers were dried over Na₂SO₄ and concentrated. The crude product was purified by silica gel flash chromatography to afford the desired enol carbonate. After purification, the major isomer is obtained with a ratio >98:2 (determined by ¹H NMR) unless stated otherwise.

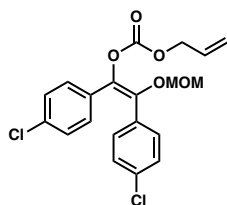
**(Z)-allyl (2-(methoxymethoxy)-1,2-diphenylvinyl) carbonate (1a)**

Run on 5.85 mmol scale. Purified by column chromatography (20% Et₂O in hexanes) to provide a white solid (1.588 g, 80% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.26 (m, 5H), 7.21 – 7.12 (m, 5H), 5.95 (ddt, *J* = 17.2, 10.5, 5.7 Hz, 1H), 5.37 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.27 (dq, *J* = 10.5, 1.3 Hz, 1H), 4.77 (s, 2H), 4.69 (dt, *J* = 5.6, 1.4 Hz, 2H), 3.56 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 153.3, 144.2, 135.8, 133.8, 132.1, 131.5, 130.4, 129.1, 128.7, 128.6, 128.1, 128.0, 118.9, 94.3, 69.0, 57.0; IR (Neat Film, NaCl) 2954, 1761, 1445, 1364, 1233, 1156, 1130, 1049, 1006, 956, 778, 698 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₂₀H₂₀NaO₅ [M+Na]⁺: 363.1203, found 363.1203.



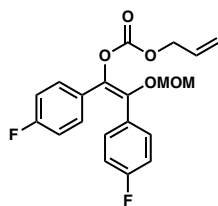
(Z)-allyl (2-(methoxymethoxy)-1,2-di-*p*-tolylvinyl) carbonate (1b)

Run on 1.19 mmol scale. Purified by column chromatography (18% Et₂O in hexanes) to provide a colorless oil (389.0 mg, 89% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.23 – 7.16 (m, 2H), 7.11 – 7.03 (m, 4H), 7.00 – 6.92 (m, 2H), 5.94 (ddt, *J* = 17.2, 10.4, 5.6 Hz, 1H), 5.37 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.26 (dq, *J* = 10.5, 1.3 Hz, 1H), 4.75 (s, 2H), 4.68 (dt, *J* = 5.6, 1.5 Hz, 2H), 3.54 (s, 3H), 2.32 (s, 3H), 2.26 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 153.4, 143.8, 139.0, 137.7, 135.6, 131.6, 131.0, 130.2, 129.3, 129.2, 128.9, 128.5, 118.8, 94.3, 69.0, 57.0, 21.5, 21.4; IR (Neat Film, NaCl) 2922 (br), 1762, 1652, 1609, 1558, 1513, 1448 (br), 1364, 1319, 1302, 1235, 1183, 1156, 1131, 1107, 1048, 1026, 1006, 961, 877, 824, 786 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₂₂H₂₈NO₅ [M+NH₄]⁺: 386.1962, found 386.1970.



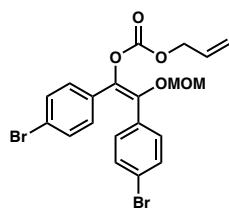
(Z)-allyl (1,2-bis(4-chlorophenyl)-2-(methoxymethoxy)vinyl) carbonate (1c)

Run on 0.573 mmol scale. Purified by column chromatography (20% Et₂O in hexanes) to provide a colorless oil (198.3 mg, 85% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.26 – 7.21 (m, 4H), 7.18 – 7.13 (m, 2H), 7.12 – 7.07 (m, 2H), 5.94 (ddt, *J* = 17.3, 10.9, 5.7 Hz, 1H), 5.38 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.29 (dq, *J* = 10.4, 1.4 Hz, 1H), 4.76 (s, 2H), 4.68 (dt, *J* = 5.8, 1.5 Hz, 2H), 3.55 (d, *J* = 0.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 153.1, 143.7, 135.4, 135.3, 134.2, 132.1, 131.6, 131.3, 130.4, 130.0, 129.1, 128.6, 119.2, 94.5, 69.3, 57.1; IR (Neat Film, NaCl) 3088, 2956, 2900, 1763, 1648, 1593, 1490, 1398, 1364, 1317, 1297, 1236, 1157, 1133, 1091, 1049, 1004, 958, 925, 874, 835, 782 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₂₀H₂₂Cl₂NO₅ [M+NH₄]⁺: 426.0870, found 426.0854.



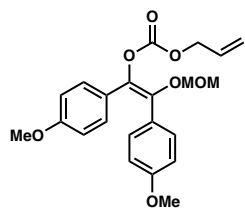
(Z)-allyl (1,2-bis(4-fluorophenyl)-2-(methoxymethoxy)vinyl) carbonate (1d)

Run on 1.25 mmol scale. Purified by column chromatography (20% Et₂O in hexanes) to provide a white solid (323.1 mg, 69% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.25 (m, 2H), 7.18 – 7.12 (m, 2H), 7.01 – 6.93 (m, 2H), 6.90 – 6.83 (m, 2H), 5.94 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.37 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.28 (dq, *J* = 10.5, 1.2 Hz, 1H), 4.76 (s, 2H), 4.68 (dt, *J* = 5.7, 1.4 Hz, 2H), 3.54 (s, 3H); ¹⁹F NMR (282 MHz, CDCl₃) δ -111.1 (dddd, *J* = 13.8, 8.7, 5.4, 1.2 Hz), -112.7 (dddd, *J* = 13.9, 8.7, 5.3, 1.3 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 163.1 (d, *J* = 250.0 Hz), 162.4 (d, *J* = 248.5 Hz), 153.2, 143.3, 135.1, 132.3 (d, *J* = 8.3 Hz), 131.4, 130.7 (d, *J* = 8.3 Hz), 129.8 (d, *J* = 3.4 Hz), 128.0 (d, *J* = 3.4 Hz), 119.1, 115.9 (d, *J* = 21.7 Hz), 115.4 (d, *J* = 21.8 Hz), 94.4, 69.2, 57.0; IR (Neat Film, NaCl) 2952, 1762, 1648, 1602, 1508, 1364, 1318, 1298, 1233, 1157, 1131, 1096, 1048, 1006, 959, 880, 841, 817, 780 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₂₀H₂₂F₂NO₅ [M+NH₄]⁺: 394.1461, found 394.1450.



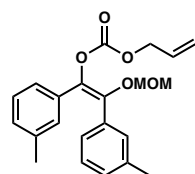
(Z)-allyl (1,2-bis(4-bromophenyl)-2-(methoxymethoxy)vinyl) carbonate (1e)

Run on 0.853 mmol scale. Purified by column chromatography (20% Et₂O in hexanes) to provide a white solid (316.2 mg, 74% yield); ¹H NMR (400 MHz CDCl₃) δ 7.45 – 7.39 (m, 2H), 7.34 – 7.28 (m, 2H), 7.21 – 7.14 (m, 2H), 7.07 – 7.01 (m, 2H), 5.94 (ddt, *J* = 17.2, 10.5, 5.7 Hz, 1H), 5.37 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.28 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.76 (s, 2H), 4.68 (dt, *J* = 5.7, 1.4 Hz, 2H), 3.54 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 153.1, 143.8, 135.4, 132.6, 132.1, 131.9, 131.6, 131.3, 130.9, 130.3, 123.8, 122.5, 119.2, 94.6, 69.3, 57.1; IR (Neat Film, NaCl) 2953 (br), 1762, 1651, 1586, 1488, 1384, 1363, 1316, 1297, 1234, 1156, 1132, 1100, 1070, 1047, 1001, 958, 872, 830, 778 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₂₀H₂₂Br₂NO₅ [M+NH₄]⁺: 513.9859, found 513.9860.



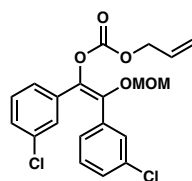
(Z)-allyl (2-(methoxymethoxy)-1,2-bis(4-methoxyphenyl)vinyl) carbonate (1f)

Run on 1.08 mmol scale. Purified by column chromatography (40% Et₂O in hexanes) to provide a slightly yellow oil (327.3 mg, 76% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.25 – 7.21 (m, 2H), 7.15 – 7.09 (m, 2H), 6.82 – 6.76 (m, 2H), 6.72 – 6.67 (m, 2H), 5.94 (ddt, *J* = 17.2, 10.5, 5.6 Hz, 1H), 5.37 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.27 (dq, *J* = 10.5, 1.3 Hz, 1H), 4.76 (s, 2H), 4.68 (dt, *J* = 5.6, 1.4 Hz, 2H), 3.79 (s, 3H), 3.75 (s, 3H), 3.55 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 160.0, 159.1, 153.4, 143.0, 135.1, 131.7, 131.6, 130.0, 126.4, 124.4, 118.8, 114.0, 113.6, 94.2, 68.9, 56.9, 55.3, 55.2; IR (Neat Film, NaCl) 2952 (br), 2838, 1761, 1608, 1511, 1458, 1364, 1319, 1292, 1237, 1175, 1156, 1130, 1107, 1049, 1017, 999, 960, 836 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₂₂H₂₈NO₇ [M+NH₄]⁺: 418.1860, found 418.1843.



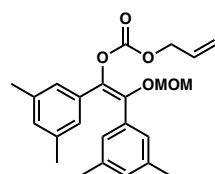
(Z)-allyl (2-(methoxymethoxy)-1,2-di-*m*-tolylvinyl) carbonate (1g)

Run on 1.18 mmol scale. Purified by column chromatography (20% Et₂O in hexanes) to provide a colorless oil (250.5 mg, 58% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.17 – 6.90 (m, 8H), 5.95 (ddt, *J* = 17.2, 10.5, 5.6 Hz, 1H), 5.38 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.28 (dq, *J* = 10.5, 1.3 Hz, 1H), 4.77 (s, 2H), 4.69 (dt, *J* = 5.6, 1.4 Hz, 2H), 3.56 (s, 3H), 2.27 (s, 2H), 2.20 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 153.3, 144.2, 138.2, 137.6, 135.8, 133.7, 132.0, 131.6, 130.8, 129.9, 129.0, 128.7, 128.4, 127.9, 127.6, 125.9, 118.9, 94.3, 69.0, 57.0, 21.4, 21.4; IR (Neat Film, NaCl) 2950, 2921, 1763, 1651, 1604, 1584, 1488, 1449, 1381, 1363, 1320, 1239, 1192, 1156, 1127, 1053, 1031, 991, 969, 926, 851, 791, 714, 695 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₂₂H₂₈NO₅ [M+NH₄]⁺: 386.1962, found 386.1973.



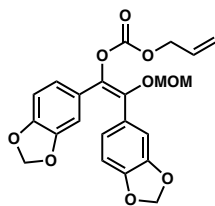
(Z)-allyl (1,2-bis(3-chlorophenyl)-2-(methoxymethoxy)vinyl) carbonate (1h)

Run on 0.397 mmol scale. Purified by column chromatography (15% Et₂O in hexanes) to provide a slightly yellow oil (101.9 mg, 63% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.34 (ddd, *J* = 2.0, 1.5, 0.5 Hz, 1H), 7.30 (ddd, *J* = 7.9, 2.1, 1.2 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.16 (dddd, *J* = 5.6, 4.5, 2.3, 1.3 Hz, 2H), 7.08 (td, *J* = 7.9, 0.5 Hz, 1H), 6.99 (ddd, *J* = 7.8, 1.7, 1.1 Hz, 1H), 5.95 (ddt, *J* = 17.1, 10.4, 5.7 Hz, 1H), 5.39 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.30 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.78 (s, 2H), 4.70 (dt, *J* = 5.7, 1.4 Hz, 2H), 3.55 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 153.0, 143.9, 135.3, 135.3, 134.7, 134.2, 133.7, 131.3, 130.1, 130.0, 129.7, 129.5, 128.7, 128.5, 127.1, 119.2, 94.6, 69.3; IR (Neat Film, NaCl) 2958 (br), 1762, 1594, 1566, 1474, 1418, 1363, 1234, 1157, 1136, 1080, 1052, 1018, 966, 792, 682 (br) cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₂₀H₂₂Cl₂NO₅ [M+NH₄]⁺: 426.0870, found 426.0859.



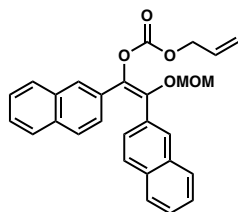
(Z)-allyl (1,2-bis(3,5-dimethylphenyl)-2-(methoxymethoxy)vinyl) carbonate (1i)

Run on 1.09 mmol scale. Purified by column chromatography (15% Et₂O in hexanes) to provide a white solid (290.7 mg, 67% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.00 – 6.87 (m, 3H), 6.87 – 6.69 (m, 3H), 5.96 (ddt, *J* = 17.2, 10.4, 5.6 Hz, 1H), 5.38 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.27 (dq, *J* = 10.5, 1.3 Hz, 1H), 4.76 (s, 2H), 4.69 (dt, *J* = 5.6, 1.5 Hz, 2H), 3.55 (s, 3H), 2.21 (s, 6H), 2.13 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 153.4, 144.1, 137.9, 137.3, 135.8, 133.6, 131.9, 131.7, 130.7, 129.6, 128.0, 126.2, 118.8, 94.3, 69.0, 56.9, 21.3, 21.3; IR (Neat Film, NaCl) 2950, 2920, 1763, 1648, 1601, 1449, 1379, 1363, 1336, 1307, 1291, 1245, 1222, 1203, 1157, 1129, 1054, 1014, 987, 952, 926, 855, 783, 682 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₂₄H₃₀NO₅ [M+NH₄]⁺: 414.2275, found 414.2260.



(Z)-allyl (1,2-bis(benzo[d][1,3]dioxol-5-yl)-2-(methoxymethoxy)vinyl) carbonate (1j)

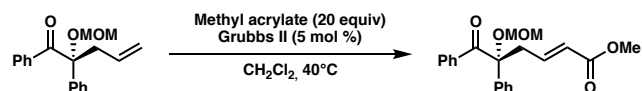
Run on 0.44 mmol scale. Purified by column chromatography (35% Et₂O in hexanes) to provide a colorless oil (188.2 mg, 99% yield); ¹H NMR (400 MHz, CDCl₃) δ 6.83 – 6.60 (m, 6H), 6.01 – 5.87 (m, 5H), 5.37 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.27 (dq, *J* = 10.5, 1.3 Hz, 1H), 4.76 (s, 2H), 4.68 (dt, *J* = 5.7, 1.4 Hz, 2H), 3.54 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 153.3, 148.3, 147.9, 147.4, 143.2, 135.2, 131.5, 127.8, 125.8, 124.7, 123.0, 119.0, 110.2, 109.1, 108.6, 108.2, 101.4, 101.2, 94.3, 69.1, 57.0; IR (Neat Film, NaCl) 2897, 1759, 1503, 1489, 1439, 1364, 1341, 1300, 1239, 1225, 1154, 1101, 1082, 1039, 1008, 968, 932, 884, 870, 812 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₂₂H₂₄NO₉ [M+NH₄]⁺: 446.1446, found 446.1452.



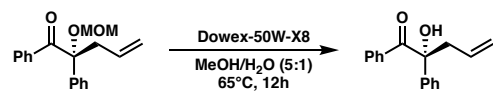
(Z)-allyl (2-(methoxymethoxy)-1,2-di(naphthalen-2-yl)vinyl) carbonate (1k)

Run on 0.988 mmol scale. Purified by column chromatography (20% Et₂O in hexanes) to provide a beige oil (345.8 mg, 79% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.87 (m, 1H), 7.86 – 7.83 (m, 1H), 7.81 – 7.76 (m, 1H), 7.74 – 7.63 (m, 4H), 7.52 – 7.36 (m, 6H), 7.15 (dd, *J* = 8.6, 1.8 Hz, 1H), 5.96 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.39 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.28 (dq, *J* = 10.5, 1.3 Hz, 1H), 4.85 (s, 2H), 4.71 (dt, *J* = 5.7, 1.4 Hz, 2H), 3.62 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 153.4, 144.6, 136.5, 133.5, 133.2, 133.1, 132.9, 131.5, 131.4, 130.2, 129.7, 128.5, 128.4, 128.4, 127.8, 127.8, 127.7, 127.6, 127.4, 127.0, 126.5, 126.5, 126.2, 119.0, 94.7, 69.2, 57.2; IR (Neat Film, NaCl) 3058, 2952, 1761, 1648, 1506, 1457, 1362, 1298, 1244, 1224, 1192, 1156, 1118, 1049, 1012, 974, 948, 862, 823, 752 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₂₈H₂₈NO₅ [M+NH₄]⁺: 458.1962, found 458.1980.

Derivatization of Alkylation Products

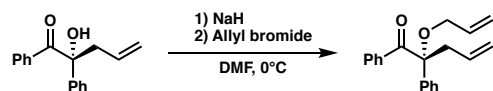
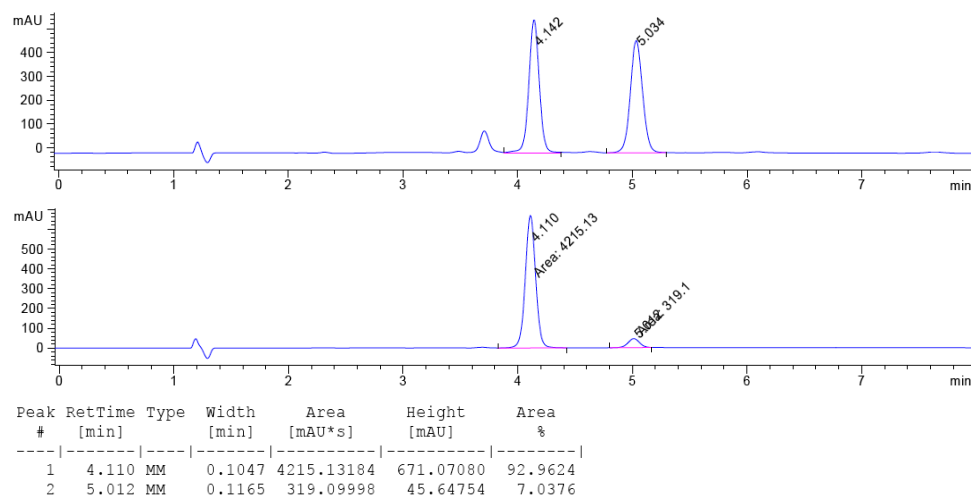
**methyl (*R,E*)-5-(methoxymethoxy)-6-oxo-5,6-diphenylhex-2-enoate (3)**

To an oven dried vial was added the alpha-tertiary benzoin (0.1 mmol) followed by CH_2Cl_2 (1 mL) and methyl acrylate (2.0 mmol, 180 μL). The resulting solution was stirred for five minutes at ambient temperature then treated with a solution of Grubbs' second generation catalyst (4.2 mg) in 500 μL CH_2Cl_2 . The reaction was then heated to 40 $^\circ\text{C}$ and stirred overnight. The crude reaction mixture was directly concentrated and then purified by silica gel flash chromatography (10% EtOAc in hexanes) to provide a colorless oil (32.0 mg, 93% yield; $[\alpha]_{\text{D}}^{25} +164.54$ (c 1.00, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.95 – 7.81 (m, 2H), 7.46 – 7.31 (m, 5H), 7.30 – 7.22 (m, 3H), 6.71 (ddd, J = 15.8, 7.8, 6.8 Hz, 1H), 5.72 (dt, J = 15.7, 1.5 Hz, 1H), 4.73 (s, 2H), 3.66 (s, 3H), 3.30 (ddd, J = 15.7, 7.7, 1.4 Hz, 1H), 3.15 (s, 3H), 3.14 – 3.08 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.0, 166.7, 143.7, 139.9, 134.5, 132.7, 130.7, 128.9, 128.2, 128.0, 125.1, 124.3, 93.6, 87.3, 57.1, 51.5, 39.7; IR (Neat Film, NaCl) 2949 (br), 1723, 1681, 1597, 1463, 1447, 1272, 1238, 1199, 1153, 1079, 1025, 926, 734, 702, 682 cm^{-1} ; HRMS (MM:ESI-APCI+) m/z calc'd for $\text{C}_{21}\text{H}_{26}\text{NO}_5$ $[\text{M}+\text{NH}_4]^+$: 372.1805, found 372.1796.

**(*S*)-2-hydroxy-1,2-diphenylpent-4-en-1-one (4)**

Dowex-50W-X8 resin (H^+ form, 170 mg) and the corresponding ketone **2a** (0.111 mmol) were added to a 1-dram vial containing 1.6 mL of MeOH and 0.32 mL of H_2O . The vial was sealed with a cap containing a PTFE-lined silicone-septum. The solution was heated and stirred at 65 $^\circ\text{C}$ for 12 h. The crude mixture was filtered through a short Celite plug to remove the solids (eluting with 1:1 hexanes:EtOAc). The resulting solution was concentrated under reduced pressure and the residue was purified by column chromatography (20% Et_2O in hexanes) to provide a white solid (27.8 mg, 99% yield); 86% ee, $[\alpha]_{\text{D}}^{25} +54.5$ (c 1.00, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 7.75 – 7.70 (m, 2H), 7.53 – 7.48 (m, 2H), 7.46 – 7.42 (m, 1H), 7.41 – 7.36 (m, 2H), 7.34 – 7.27 (m, 3H), 5.74 (dddd, J = 17.1, 10.2, 7.5, 6.9 Hz, 1H), 5.12 (ddt, J = 10.2, 1.9, 0.9 Hz, 1H), 5.02 (ddt, J = 17.2, 2.0, 1.3 Hz, 1H), 4.19 (s, 1H), 3.15 (ddt, J = 13.8, 7.5, 1.0 Hz,

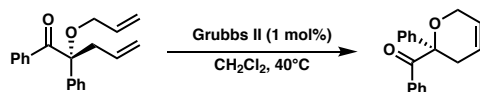
¹H), 2.98 (ddt, $J = 13.7, 6.9, 1.2$ Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 200.9, 141.9, 134.6, 132.9, 132.4, 130.3, 129.0, 128.3, 128.2, 125.8, 120.5, 81.5, 44.1; IR (Neat Film, NaCl) 3459 (Br), 3062, 2924, 1674, 1597, 1578, 1491, 1447, 1364, 1230, 1181, 1140, 1096, 1068, 1035, 1001, 976, 922, 762, 724, 699, 678, 632 cm⁻¹; HRMS (MM:ESI-APCI+) m/z calc'd for C₁₇H₁₅O [M-OH]⁺: 235.1117, found 235.1118; SFC Conditions: 10% IPA, 2.5 mL/min, Chiralcel OD-H column, $\lambda = 210$ nm, t_R (min): major = 4.11, minor = 5.01.



(*R*)-2-(allyloxy)-1,2-diphenylpent-4-en-1-one (SI1)

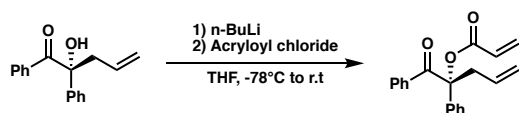
To a solution of **4** in DMF (3 mL) was added NaH (0.6 mmol) at 0 °C. The mixture was stirred for 30 min at 0 °C then allyl bromide (0.39 mmol) was added dropwise and the reaction was allowed to warm-up to room temperature. After completion of the reaction showed by TLC, NH₄Cl (aq) was added and the mixture was extracted with EtOAc three times. The combined organic layers were washed with water, brine, dried over Na₂SO₄, filtered and concentrated. The crude product was purified by silica gel flash chromatography (2% EtOAc in hexanes) to afford the desired product as a colorless oil (77.2 mg, 88% yield); $[\alpha]_D^{25} +52.3$ (c 1.00, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.94 (m, 2H), 7.52 – 7.45 (m, 2H), 7.44 – 7.37 (m, 1H), 7.36 – 7.30 (m, 2H), 7.29 – 7.21 (m, 3H), 5.75 (dddd, $J = 17.2, 10.5, 5.6, 5.0$ Hz, 1H), 5.60 – 5.47 (m, 1H), 5.22 (dq, $J = 17.2, 1.7$ Hz, 1H), 5.08 (dq, $J = 10.4, 1.5$ Hz, 1H), 5.01 – 4.98 (m, 1H), 4.98 – 4.91 (m, 1H), 4.16 (ddt, $J = 11.9, 5.6, 1.5$ Hz, 1H), 3.72 (ddt, $J = 11.9, 5.0, 1.6$ Hz, 1H), 3.16 (ddt, $J = 15.4, 7.6, 1.2$ Hz, 1H), 2.91 (ddt, $J = 15.4, 6.4, 1.6$ Hz, 1H); ¹³C NMR (100 MHz,

CDCl₃) δ 200.9, 140.7, 135.0, 134.1, 132.8, 132.4, 130.3, 128.5, 128.1, 127.6, 125.5, 118.3, 116.8, 87.6, 65.4, 40.0; IR (Neat Film, NaCl) 3072, 2935, 1681, 1647, 1596, 1447, 1238, 1120, 1072, 1028, 994, 918, 827, 730, 701, 681, 667 cm⁻¹; HRMS (MM:ESI-APCI+) m/z calc'd for C₂₀H₂₀O₂Na [M+Na]⁺: 315.1356, found 315.1343.



(R)-phenyl(2-phenyl-3,6-dihydro-2H-pyran-2-yl)methanone (5)

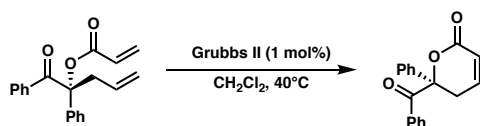
To an oven dried vial was added **5** (0.24 mmol) followed by CH₂Cl₂ (3 mL). The resulting solution was treated with a solution of Grubbs' second-generation catalyst (2 mg) in CH₂Cl₂ (1.5 mL). The reaction was then heated to 40 °C and stirred overnight. The crude reaction mixture was directly concentrated and then purified by silica gel flash chromatography (3% EtOAc in hexanes) to provide a colorless oil (64.2 mg, 99% yield); [α]_D²⁵ +222.8 (*c* 1.00, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.04 – 7.97 (m, 2H), 7.55 – 7.49 (m, 2H), 7.47 – 7.40 (m, 1H), 7.39 – 7.33 (m, 2H), 7.33 – 7.26 (m, 3H), 5.92 (ddq, *J* = 10.2, 5.7, 2.2 Hz, 1H), 5.70 – 5.59 (m, 1H), 4.33 (dtdd, *J* = 17.2, 3.2, 2.2, 1.0 Hz, 1H), 4.05 (dddt, *J* = 17.2, 4.1, 3.0, 2.1 Hz, 1H), 3.27 – 3.15 (m, 1H), 2.23 (ddtd, *J* = 17.3, 4.1, 3.0, 2.2 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 199.6, 142.4, 135.1, 132.8, 130.0, 128.9, 128.2, 127.6, 124.5, 124.4, 124.2, 84.2, 63.7, 35.0; IR (Neat Film, NaCl) 3059, 3037, 2931, 2900, 2840, 1682, 1597, 1579, 1492, 1447, 1417, 1386, 1327, 1258, 1226, 1210, 1180, 1089, 1024, 978, 960, 942, 793, 754, 700, 657 cm⁻¹; HRMS (MM:ESI-APCI+) m/z calc'd for C₁₈H₁₇O₂ [M+H]⁺: 265.1223, found 265.1224.



(R)-1-oxo-1,2-diphenylpent-4-en-2-yl acrylate (SI2)

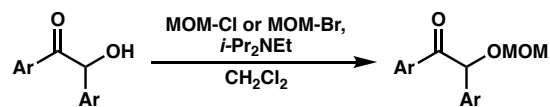
To a solution of **4** (0.147 mmol) in THF (1.5 mL) was added dropwise *n*-BuLi (0.127 mL, 2.3M solution in hexane, 0.294 mmol, 2 equiv) at –78 °C. The resulting yellow solution was stirred for 30 min at –78 °C. Acryloyl chloride (0.735 mmol) was then added dropwise and the reaction was allowed to warm-up to room temperature overnight. Water was added and the reaction was extracted three times with EtOAc. The combined organic layers were washed with 1N NaOH (aq), brine, dried over Na₂SO₄, filtered and concentrated. The crude product was purified by

silica gel flash chromatography (5% EtOAc in hexanes) to afford the desired product as a colorless oil (42.2 mg, 94% yield); $[\alpha]_D^{25} +140.6$ (*c* 1.00, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.74 – 7.69 (m, 2H), 7.60 – 7.54 (m, 2H), 7.45 – 7.38 (m, 2H), 7.38 – 7.29 (m, 2H), 7.23 (ddt, *J* = 8.0, 6.7, 1.2 Hz, 2H), 6.40 (dd, *J* = 17.3, 1.3 Hz, 1H), 6.12 (dd, *J* = 17.3, 10.5 Hz, 1H), 5.83 (dd, *J* = 10.4, 1.3 Hz, 1H), 5.46 (dddd, *J* = 17.0, 10.3, 8.8, 5.9 Hz, 1H), 5.02 – 4.87 (m, 2H), 3.60 – 3.41 (m, 1H), 3.13 (ddt, *J* = 14.8, 5.9, 1.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 196.4, 164.2, 137.8, 135.1, 132.3, 132.0, 131.6, 129.2, 129.0, 128.2, 128.2, 128.0, 125.0, 119.4, 88.3, 41.9; IR (Neat Film, NaCl) 3060, 2929, 1727, 1687, 1634, 1598, 1491, 1447, 1404, 1295, 1243, 1173, 1121, 1061, 1028, 986, 919, 828, 809, 760, 736, 701, 688, 681 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₂₀H₂₂NO₃ [M+NH₄]⁺: 324.1594, found 324.1597.



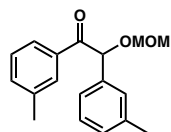
(*R*)-6-benzoyl-6-phenyl-5,6-dihydro-2*H*-pyran-2-one (6)

In an oven dried vial, a solution of **7** (0.078 mmol) in CH₂Cl₂ (1.1 mL) was treated with a solution of Grubbs' second-generation catalyst (0.6 mg) in CH₂Cl₂ (0.5 mL). The reaction was then heated to 40 °C and stirred overnight. The crude reaction mixture was directly concentrated and then purified by silica gel flash chromatography (10% EtOAc in hexanes) to provide a colorless oil (21.5 mg, 99% yield); $[\alpha]_D^{25} +344.7$ (*c* 1.00, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.87 (m, 2H), 7.61 – 7.56 (m, 2H), 7.48 – 7.38 (m, 3H), 7.38 – 7.28 (m, 3H), 6.95 (ddd, *J* = 9.9, 5.9, 2.5 Hz, 1H), 5.97 (ddd, *J* = 9.9, 2.7, 0.9 Hz, 1H), 3.65 (ddd, *J* = 18.2, 5.9, 1.0 Hz, 1H), 2.70 (dt, *J* = 18.2, 2.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 196.9, 162.3, 146.3, 138.4, 134.0, 133.5, 130.7, 129.3, 128.8, 128.5, 124.4, 120.9, 90.4, 34.9; IR (Neat Film, NaCl) 3061, 2924, 2854, 1744, 1682, 1596, 1579, 1491, 1448, 1409, 1378, 1319, 1244, 1222, 1184, 1158, 1100, 1056, 1002, 951, 909, 868, 815, 784, 755, 736, 699 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₁₈H₁₈NO₃ [M+NH₄]⁺: 296.1281, found 296.1280.

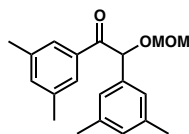
Mom protection of benzoin derivatives

Method A: At room temperature, MOM-Br (4 equiv) was added to a solution of corresponding benzoin (1 equiv) and *i*-Pr₂NEt (5 equiv) in CH₂Cl₂ (0.25 mol/L). The reaction was stirred overnight at 40 °C. The crude reaction mixture was quenched with the addition of a 2 M NaOH solution. The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ twice. The combined organic layers were washed with a 1 M HCl solution, dried over Na₂SO₄ and concentrated. The crude product was purified by silica gel flash chromatography to afford the desired Mom protected benzoin.

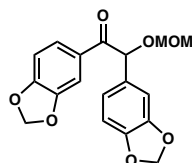
Method B: At 0 °C, MOM-Cl (4 equiv) was added to a solution of corresponding benzoin (1 equiv) and *i*-Pr₂NEt (5 equiv) in CH₂Cl₂ (0.25 mol/L). The reaction was stirred overnight at room temperature. The crude reaction mixture was quenched with the addition of a 2 M NaOH solution. The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ twice. The combined organic layers were washed with a 1 M HCl solution, dried over Na₂SO₄ and concentrated. The crude product was purified by silica gel flash chromatography to afford the desired Mom protected benzoin.

**2-(methoxymethoxy)-1,2-di-*m*-tolylethan-1-one (SI3)**

Method A. Run on 2.31 mmol scale. Purified by column chromatography (20% Et₂O in hexanes) to provide a colorless oil (415.3 mg, 75% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.78 (s, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.32 – 7.19 (m, 5H), 7.08 (d, *J* = 7.4 Hz, 1H), 5.97 (s, 1H), 4.74 (s, 2H), 3.36 (s, 3H), 2.34 (s, 3H), 2.31 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 196.8, 138.9, 138.5, 135.9, 135.3, 134.2, 129.6, 129.6, 128.9, 128.7, 128.5, 126.4, 125.4, 95.1, 79.9, 56.1, 21.5, 21.5; IR (Neat Film, NaCl) 2926 (br), 1694, 1604, 1586, 1487, 1457, 1254, 1213, 1167, 1149, 1108, 1034, 964, 918, 773, 700 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₁₈H₂₁O₃ [M+H]⁺: 285.1485, found 285.1484.


1,2-bis(3,5-dimethylphenyl)-2-(methoxymethoxy)ethan-1-one (SI4)

Method A. Run on 1.49 mmol scale. Purified by column chromatography (20% Et₂O in hexanes) to provide a colorless oil (411.1 mg, 88% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.58 (s, 2H), 7.13 (s, 1H), 7.07 (s, 2H), 6.92 (s, 1H), 5.96 (s, 1H), 4.76 – 4.72 (m, 2H), 3.39 (s, 3H), 2.32 (s, 6H), 2.28 (s, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 196.9, 138.6, 138.2, 135.8, 135.4, 135.0, 130.5, 126.8, 126.0, 95.0, 79.6, 56.1, 21.4, 21.3; IR (Neat Film, NaCl) 2920 (br), 1691, 1606, 1457 br, 1305, 1184, 1149, 1107, 1043, 1017, 918, 848, 792 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₂₀H₂₅O₃ [M+H]⁺: 313.1798, found 313.1804.


1,2-bis(benzo[d][1,3]dioxol-5-yl)-2-(methoxymethoxy)ethan-1-one (SI5)

Method B. Run on 1.73 mmol scale. Purified by column chromatography (50% Et₂O in hexanes) to provide a beige amorphous solid (571.3 mg, 96% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.59 (ddd, *J* = 8.2, 1.8, 0.6 Hz, 1H), 7.44 (d, *J* = 1.7 Hz, 1H), 6.94 – 6.89 (m, 2H), 6.82 – 6.73 (m, 2H), 6.00 (s, 2H), 5.94 – 5.92 (m, 2H), 5.83 (s, 1H), 4.72 (s, 2H), 3.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 194.4, 152.0, 148.3, 148.2, 148.1, 130.0, 129.8, 125.5, 122.1, 108.9, 108.7, 108.3, 108.1, 102.0, 101.4, 94.9, 79.3, 56.1; IR (Neat Film, NaCl) 2896, 1684, 1604, 1503, 1489, 1443, 1358, 1251, 1150, 1099, 1037, 931, 798 cm⁻¹; HRMS (MM:ESI-APCI+) *m/z* calc'd for C₁₈H₁₇O₇ [M+H]⁺: 345.0969, found 345.0963.

X-Ray Crystal Structure for 4

A crystal of compound **4** was grown by slow evaporation of EtOAc/Hexanes.

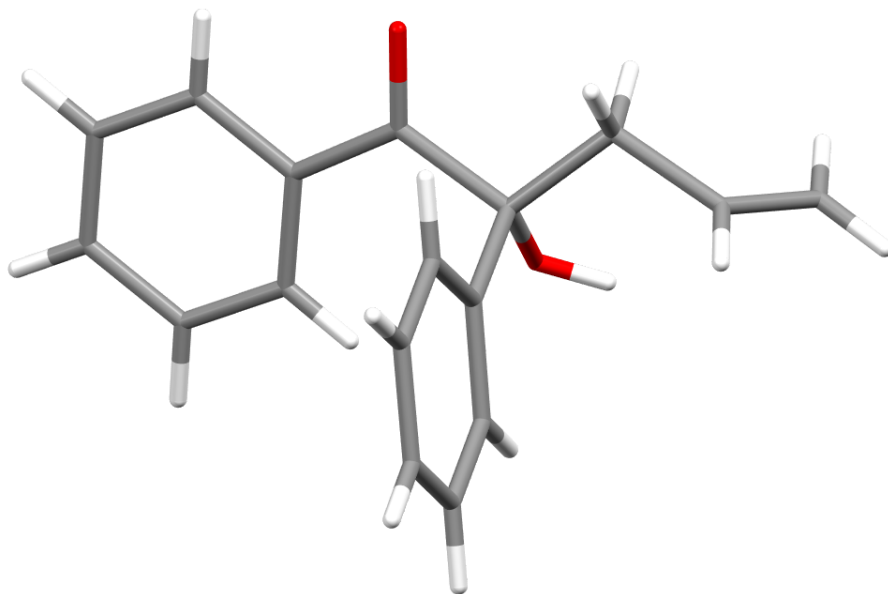
Figure S1. X-Ray Coordinate of compound 4

Table 1. Crystal data and structure refinement for v19245.

| | | |
|---------------------------------|--|-----------------|
| Identification code | v19245 | |
| Empirical formula | C ₁₇ H ₁₆ O ₂ | |
| Formula weight | 252.30 | |
| Temperature | 100 K | |
| Wavelength | 1.54178 Å | |
| Crystal system | Triclinic | |
| Space group | P1 | |
| Unit cell dimensions | a = 6.0838(9) Å | a = 104.527(6)° |
| | b = 7.2384(11) Å | b = 95.732(7)° |
| | c = 8.3465(12) Å | g = 105.236(7)° |
| Volume | 337.85(9) Å ³ | |
| Z | 1 | |
| Density (calculated) | 1.240 g/cm ³ | |
| Absorption coefficient | 0.635 mm ⁻¹ | |
| F(000) | 134 | |
| Crystal size | 0.23 x 0.22 x 0.09 mm ³ | |
| Theta range for data collection | 5.564 to 79.408°. | |

| | |
|---|---|
| Index ranges | -7<= <i>h</i> <=7,-9<= <i>k</i> <=9,-10<= <i>l</i> <=10 |
| Reflections collected | 15392 |
| Independent reflections | 2730 [R(int) = 0.0394] |
| Completeness to $\theta = 67.679^\circ$ | 100.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.0000 and 0.8971 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 2730 / 3 / 173 |
| Goodness-of-fit on F^2 | 1.124 |
| Final R indices [$I > 2\sigma(I)$] | R1 = 0.0347, wR2 = 0.1003 |
| R indices (all data) | R1 = 0.0350, wR2 = 0.1008 |
| Absolute structure parameter [Flack] | -0.08(12) |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.237 and -0.195 e. \AA^{-3} |

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for v19245. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| | x | y | z | $U(\text{eq})$ |
|-------|----------|----------|---------|----------------|
| O(1) | 1929(3) | 6639(2) | 3788(2) | 28(1) |
| O(2) | 7109(2) | 5729(2) | 3722(2) | 18(1) |
| C(1) | 3498(4) | 2012(3) | 2629(3) | 19(1) |
| C(2) | 2477(4) | 21(3) | 1703(3) | 23(1) |
| C(3) | 196(4) | -625(4) | 867(3) | 25(1) |
| C(4) | -1054(4) | 738(4) | 941(3) | 26(1) |
| C(5) | -46(4) | 2728(3) | 1848(3) | 21(1) |
| C(6) | 2246(4) | 3391(3) | 2708(3) | 18(1) |
| C(7) | 3157(4) | 5550(3) | 3727(3) | 17(1) |
| C(8) | 5633(3) | 6424(3) | 4782(3) | 16(1) |
| C(9) | 5597(4) | 5646(3) | 6333(3) | 17(1) |
| C(10) | 7086(4) | 4584(3) | 6704(3) | 18(1) |
| C(11) | 7052(4) | 3930(3) | 8137(3) | 22(1) |
| C(12) | 5520(4) | 4327(4) | 9212(3) | 25(1) |
| C(13) | 4017(4) | 5365(4) | 8842(3) | 24(1) |
| C(14) | 4053(4) | 6033(3) | 7417(3) | 20(1) |
| C(15) | 6325(4) | 8725(3) | 5307(3) | 20(1) |
| C(16) | 8745(4) | 9622(3) | 6294(3) | 20(1) |
| C(17) | 10493(4) | 10636(4) | 5752(3) | 27(1) |

Table 3. Bond lengths [Å] and angles [°] for v19245.

| | |
|--------------|----------|
| O(1)-C(7) | 1.216(3) |
| O(2)-H(2W) | 0.8400 |
| O(2)-C(8) | 1.420(3) |
| C(1)-H(1) | 0.9500 |
| C(1)-C(2) | 1.391(3) |
| C(1)-C(6) | 1.399(3) |
| C(2)-H(2) | 0.9500 |
| C(2)-C(3) | 1.390(3) |
| C(3)-H(3) | 0.9500 |
| C(3)-C(4) | 1.389(4) |
| C(4)-H(4) | 0.9500 |
| C(4)-C(5) | 1.386(3) |
| C(5)-H(5) | 0.9500 |
| C(5)-C(6) | 1.402(3) |
| C(6)-C(7) | 1.502(3) |
| C(7)-C(8) | 1.549(3) |
| C(8)-C(9) | 1.535(3) |
| C(8)-C(15) | 1.540(3) |
| C(9)-C(10) | 1.392(3) |
| C(9)-C(14) | 1.401(3) |
| C(10)-H(10) | 0.9500 |
| C(10)-C(11) | 1.393(3) |
| C(11)-H(11) | 0.9500 |
| C(11)-C(12) | 1.391(4) |
| C(12)-H(12) | 0.9500 |
| C(12)-C(13) | 1.384(4) |
| C(13)-H(13) | 0.9500 |
| C(13)-C(14) | 1.392(3) |
| C(14)-H(14) | 0.9500 |
| C(15)-H(15A) | 0.9900 |
| C(15)-H(15B) | 0.9900 |
| C(15)-C(16) | 1.502(3) |
| C(16)-H(16) | 0.9500 |
| C(16)-C(17) | 1.314(3) |

| | |
|------------------|------------|
| C(17)-H(17A) | 0.9500 |
| C(17)-H(17B) | 0.9500 |
| C(8)-O(2)-H(2W) | 109.5 |
| C(2)-C(1)-H(1) | 119.9 |
| C(2)-C(1)-C(6) | 120.2(2) |
| C(6)-C(1)-H(1) | 119.9 |
| C(1)-C(2)-H(2) | 119.8 |
| C(3)-C(2)-C(1) | 120.5(2) |
| C(3)-C(2)-H(2) | 119.8 |
| C(2)-C(3)-H(3) | 120.2 |
| C(4)-C(3)-C(2) | 119.5(2) |
| C(4)-C(3)-H(3) | 120.2 |
| C(3)-C(4)-H(4) | 119.8 |
| C(5)-C(4)-C(3) | 120.4(2) |
| C(5)-C(4)-H(4) | 119.8 |
| C(4)-C(5)-H(5) | 119.8 |
| C(4)-C(5)-C(6) | 120.5(2) |
| C(6)-C(5)-H(5) | 119.8 |
| C(1)-C(6)-C(5) | 118.9(2) |
| C(1)-C(6)-C(7) | 124.26(18) |
| C(5)-C(6)-C(7) | 116.77(19) |
| O(1)-C(7)-C(6) | 120.41(19) |
| O(1)-C(7)-C(8) | 118.4(2) |
| C(6)-C(7)-C(8) | 121.18(17) |
| O(2)-C(8)-C(7) | 106.12(16) |
| O(2)-C(8)-C(9) | 112.43(17) |
| O(2)-C(8)-C(15) | 110.40(17) |
| C(9)-C(8)-C(7) | 107.21(17) |
| C(9)-C(8)-C(15) | 110.82(17) |
| C(15)-C(8)-C(7) | 109.68(16) |
| C(10)-C(9)-C(8) | 121.64(19) |
| C(10)-C(9)-C(14) | 118.92(19) |
| C(14)-C(9)-C(8) | 119.43(19) |
| C(9)-C(10)-H(10) | 119.7 |
| C(9)-C(10)-C(11) | 120.5(2) |

| | |
|---------------------|------------|
| C(11)-C(10)-H(10) | 119.7 |
| C(10)-C(11)-H(11) | 119.9 |
| C(12)-C(11)-C(10) | 120.3(2) |
| C(12)-C(11)-H(11) | 119.9 |
| C(11)-C(12)-H(12) | 120.2 |
| C(13)-C(12)-C(11) | 119.6(2) |
| C(13)-C(12)-H(12) | 120.2 |
| C(12)-C(13)-H(13) | 119.8 |
| C(12)-C(13)-C(14) | 120.4(2) |
| C(14)-C(13)-H(13) | 119.8 |
| C(9)-C(14)-H(14) | 119.9 |
| C(13)-C(14)-C(9) | 120.3(2) |
| C(13)-C(14)-H(14) | 119.9 |
| C(8)-C(15)-H(15A) | 109.4 |
| C(8)-C(15)-H(15B) | 109.4 |
| H(15A)-C(15)-H(15B) | 108.0 |
| C(16)-C(15)-C(8) | 111.06(18) |
| C(16)-C(15)-H(15A) | 109.4 |
| C(16)-C(15)-H(15B) | 109.4 |
| C(15)-C(16)-H(16) | 118.0 |
| C(17)-C(16)-C(15) | 124.1(2) |
| C(17)-C(16)-H(16) | 118.0 |
| C(16)-C(17)-H(17A) | 120.0 |
| C(16)-C(17)-H(17B) | 120.0 |
| H(17A)-C(17)-H(17B) | 120.0 |

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for v19245. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

| | U^{11} | U^{22} | U^{33} | U^{23} | U^{13} | U^{12} |
|-------|----------|----------|----------|----------|----------|----------|
| O(1) | 16(1) | 22(1) | 44(1) | 7(1) | 1(1) | 8(1) |
| O(2) | 13(1) | 22(1) | 19(1) | 4(1) | 6(1) | 4(1) |
| C(1) | 18(1) | 18(1) | 18(1) | 6(1) | 3(1) | 4(1) |
| C(2) | 26(1) | 21(1) | 22(1) | 6(1) | 5(1) | 9(1) |
| C(3) | 28(1) | 21(1) | 21(1) | 0(1) | 4(1) | 3(1) |
| C(4) | 18(1) | 31(1) | 21(1) | 1(1) | -1(1) | 3(1) |
| C(5) | 18(1) | 26(1) | 20(1) | 4(1) | 2(1) | 8(1) |
| C(6) | 16(1) | 22(1) | 15(1) | 7(1) | 4(1) | 5(1) |
| C(7) | 14(1) | 18(1) | 22(1) | 10(1) | 5(1) | 4(1) |
| C(8) | 14(1) | 17(1) | 19(1) | 6(1) | 6(1) | 6(1) |
| C(9) | 16(1) | 15(1) | 18(1) | 3(1) | 3(1) | 2(1) |
| C(10) | 18(1) | 19(1) | 19(1) | 4(1) | 3(1) | 7(1) |
| C(11) | 24(1) | 18(1) | 21(1) | 4(1) | -1(1) | 6(1) |
| C(12) | 28(1) | 25(1) | 16(1) | 5(1) | 1(1) | 2(1) |
| C(13) | 25(1) | 23(1) | 19(1) | 2(1) | 9(1) | 3(1) |
| C(14) | 20(1) | 19(1) | 22(1) | 4(1) | 5(1) | 6(1) |
| C(15) | 18(1) | 17(1) | 25(1) | 7(1) | 4(1) | 5(1) |
| C(16) | 23(1) | 18(1) | 18(1) | 4(1) | 3(1) | 6(1) |
| C(17) | 21(1) | 24(1) | 27(1) | 1(1) | 4(1) | 1(1) |

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for v19245.

| | x | y | z | U(eq) |
|--------|-------|-------|-------|-------|
| H(2W) | 8466 | 6502 | 4056 | 28 |
| H(1) | 5051 | 2437 | 3210 | 22 |
| H(2) | 3344 | -903 | 1642 | 27 |
| H(3) | -502 | -1990 | 248 | 31 |
| H(4) | -2611 | 303 | 366 | 31 |
| H(5) | -913 | 3650 | 1887 | 26 |
| H(10) | 8134 | 4303 | 5974 | 22 |
| H(11) | 8078 | 3209 | 8381 | 26 |
| H(12) | 5506 | 3889 | 10194 | 30 |
| H(13) | 2955 | 5622 | 9566 | 28 |
| H(14) | 3025 | 6755 | 7179 | 24 |
| H(15A) | 6221 | 9189 | 4291 | 23 |
| H(15B) | 5234 | 9184 | 5999 | 23 |
| H(16) | 9030 | 9446 | 7378 | 24 |
| H(17A) | 10264 | 10838 | 4674 | 32 |
| H(17B) | 11985 | 11166 | 6438 | 32 |

Table 6. Torsion angles [°] for v19245.

| | |
|-------------------------|-------------|
| O(1)-C(7)-C(8)-O(2) | -136.5(2) |
| O(1)-C(7)-C(8)-C(9) | 103.2(2) |
| O(1)-C(7)-C(8)-C(15) | -17.2(3) |
| O(2)-C(8)-C(9)-C(10) | 7.1(3) |
| O(2)-C(8)-C(9)-C(14) | -173.72(18) |
| O(2)-C(8)-C(15)-C(16) | -61.9(2) |
| C(1)-C(2)-C(3)-C(4) | 0.9(4) |
| C(1)-C(6)-C(7)-O(1) | -176.9(2) |
| C(1)-C(6)-C(7)-C(8) | 0.5(3) |
| C(2)-C(1)-C(6)-C(5) | 0.3(3) |
| C(2)-C(1)-C(6)-C(7) | 177.4(2) |
| C(2)-C(3)-C(4)-C(5) | -0.3(4) |
| C(3)-C(4)-C(5)-C(6) | -0.2(3) |
| C(4)-C(5)-C(6)-C(1) | 0.3(3) |
| C(4)-C(5)-C(6)-C(7) | -177.1(2) |
| C(5)-C(6)-C(7)-O(1) | 0.3(3) |
| C(5)-C(6)-C(7)-C(8) | 177.67(19) |
| C(6)-C(1)-C(2)-C(3) | -0.9(3) |
| C(6)-C(7)-C(8)-O(2) | 46.1(2) |
| C(6)-C(7)-C(8)-C(9) | -74.3(2) |
| C(6)-C(7)-C(8)-C(15) | 165.33(18) |
| C(7)-C(8)-C(9)-C(10) | 123.4(2) |
| C(7)-C(8)-C(9)-C(14) | -57.5(2) |
| C(7)-C(8)-C(15)-C(16) | -178.45(18) |
| C(8)-C(9)-C(10)-C(11) | 178.69(19) |
| C(8)-C(9)-C(14)-C(13) | -179.09(19) |
| C(8)-C(15)-C(16)-C(17) | 112.5(2) |
| C(9)-C(8)-C(15)-C(16) | 63.4(2) |
| C(9)-C(10)-C(11)-C(12) | 0.2(3) |
| C(10)-C(9)-C(14)-C(13) | 0.1(3) |
| C(10)-C(11)-C(12)-C(13) | 0.5(3) |
| C(11)-C(12)-C(13)-C(14) | -0.9(3) |
| C(12)-C(13)-C(14)-C(9) | 0.6(3) |
| C(14)-C(9)-C(10)-C(11) | -0.5(3) |

| | |
|-----------------------|-----------|
| C(15)-C(8)-C(9)-C(10) | -117.0(2) |
| C(15)-C(8)-C(9)-C(14) | 62.2(2) |

Table 7. Hydrogen bonds for v19245 [\AA and $^\circ$].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | $\angle(\text{DHA})$ |
|---------------------|--------|----------|----------|----------------------|
| O(2)-H(2W)...O(1)#1 | 0.84 | 2.12 | 2.823(2) | 141.1 |

References

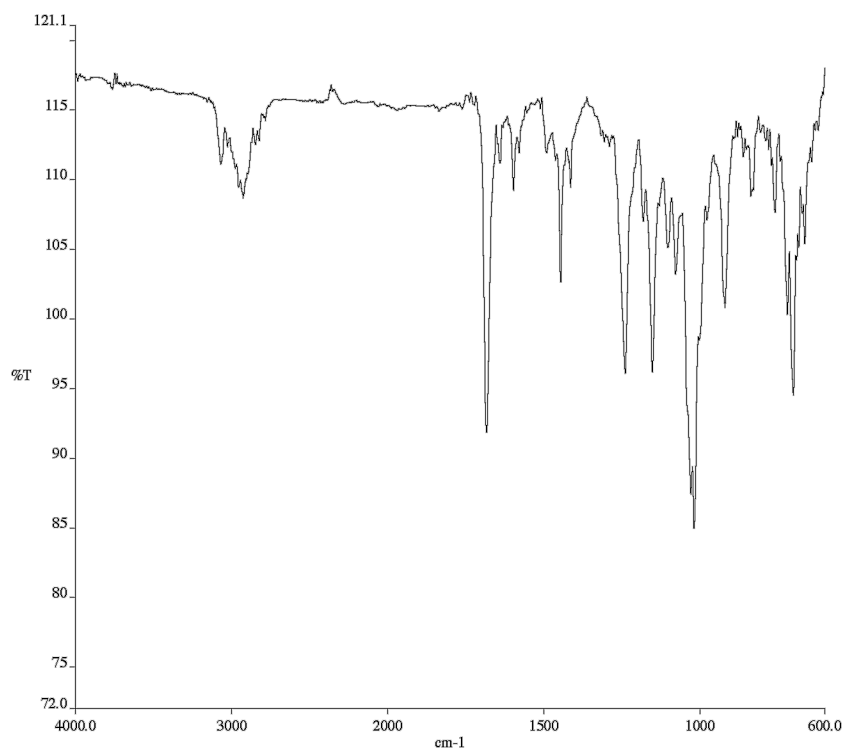
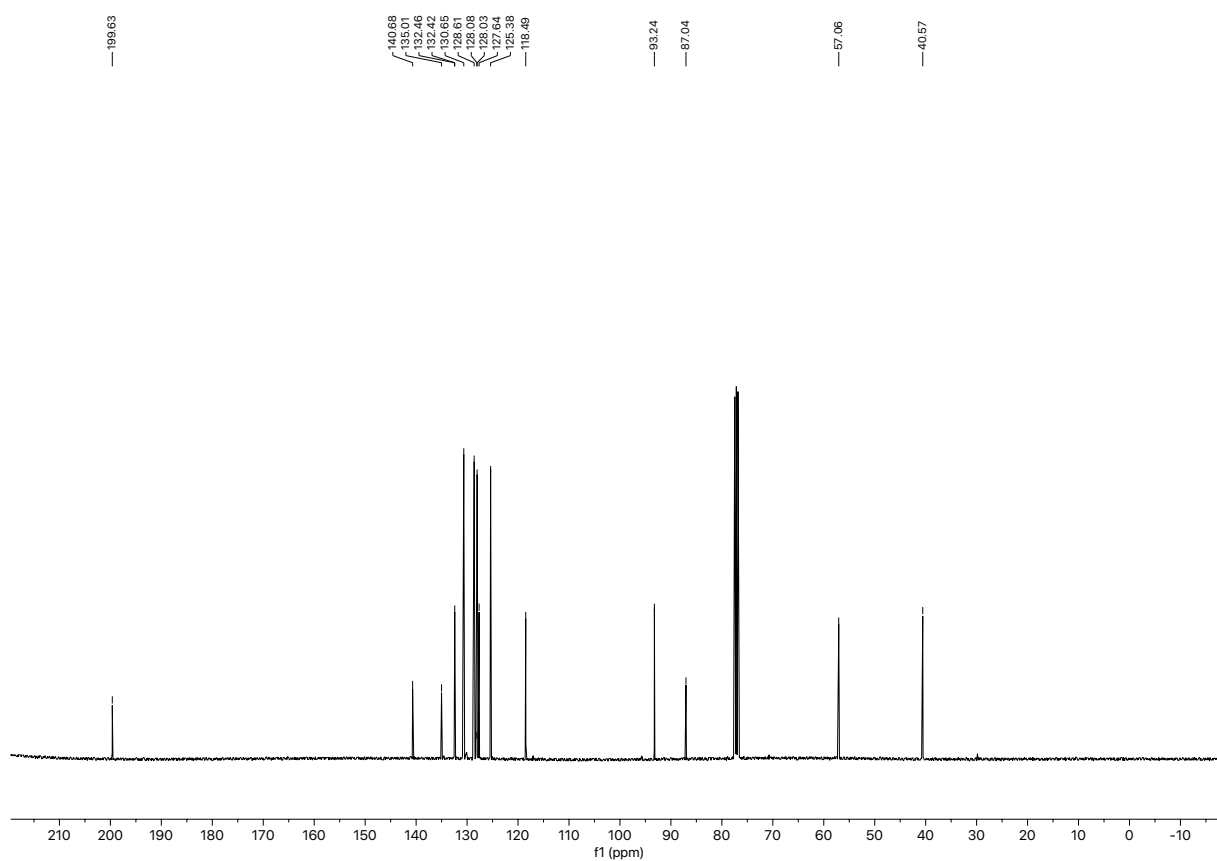
- (1) Pangborn, A. M.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.
- (2) Trost, B. M.; Van Vranken, D. L.; Bingel, C. *J. Am. Chem. Soc.* **1992**, *114*, 9327–9343.
- (3) Meng, J.; Gao, M.; Lv, H.; Zhang, X. *Org. Lett.* **2015**, *178*, 1842-1845

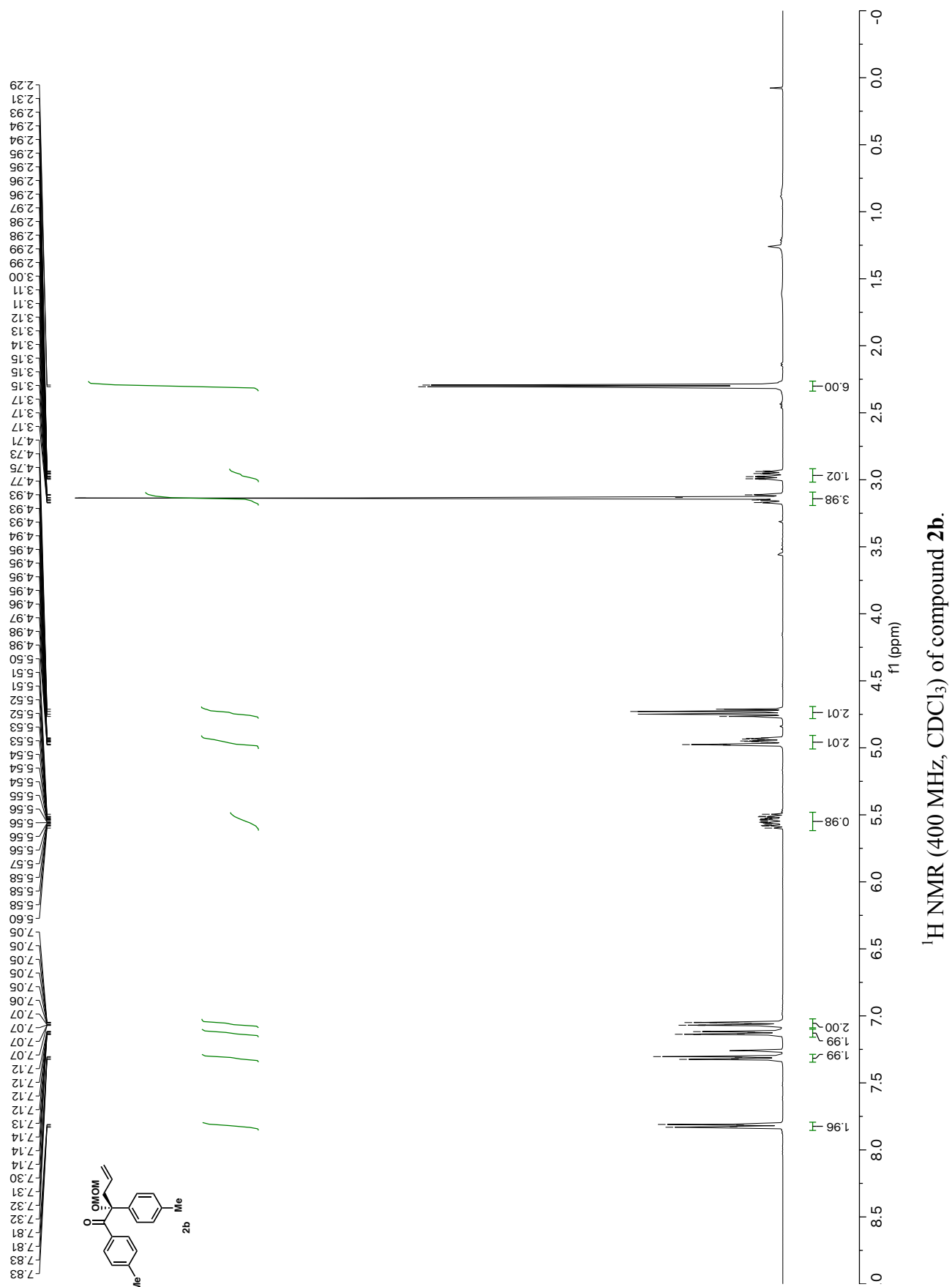
¹H NMR (400 MHz, CDCl₃) of compound **2a.**

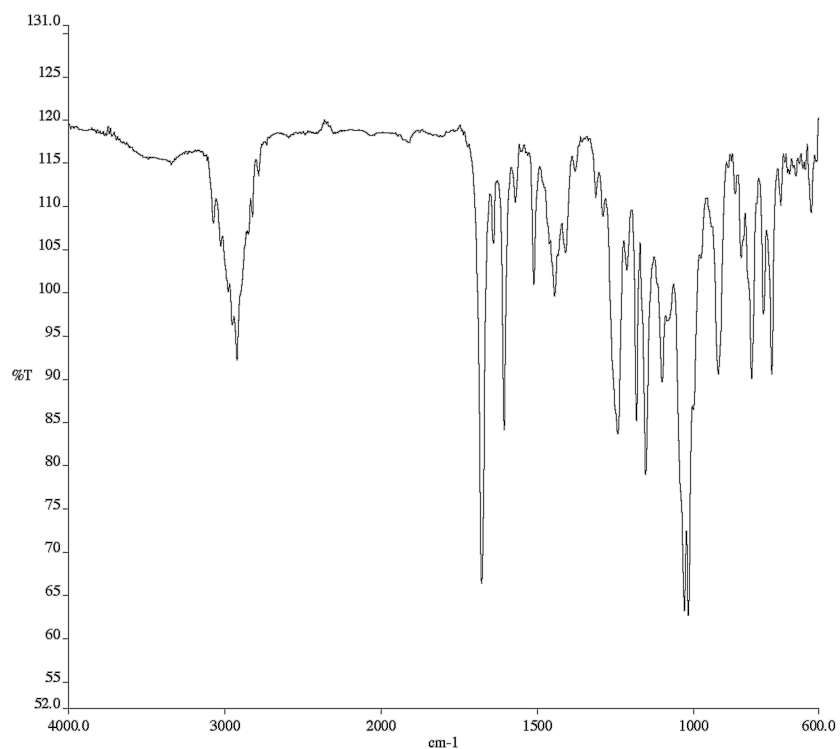
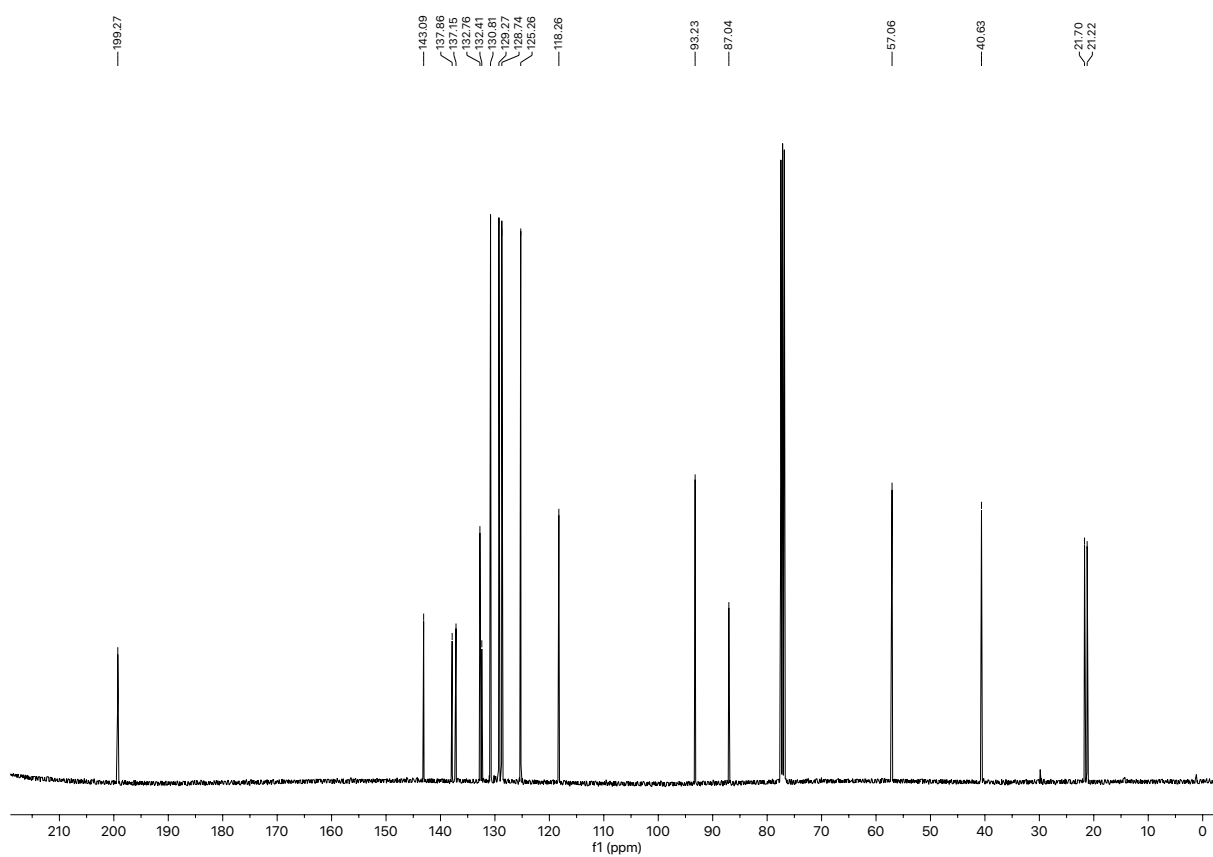
Chemical structure of **2a** is shown in the top left corner.

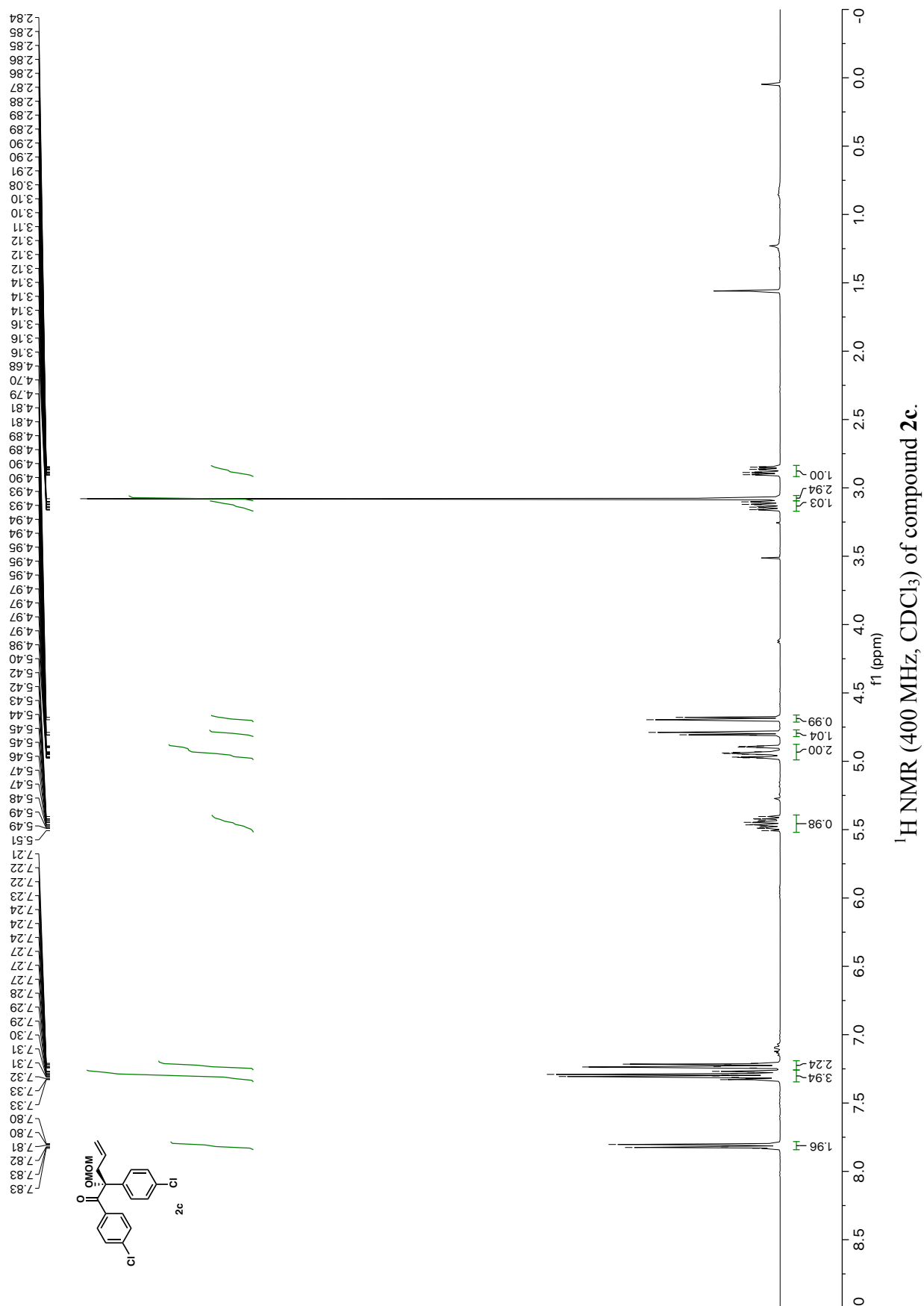
The spectrum displays the following chemical shifts (ppm) and integration values:

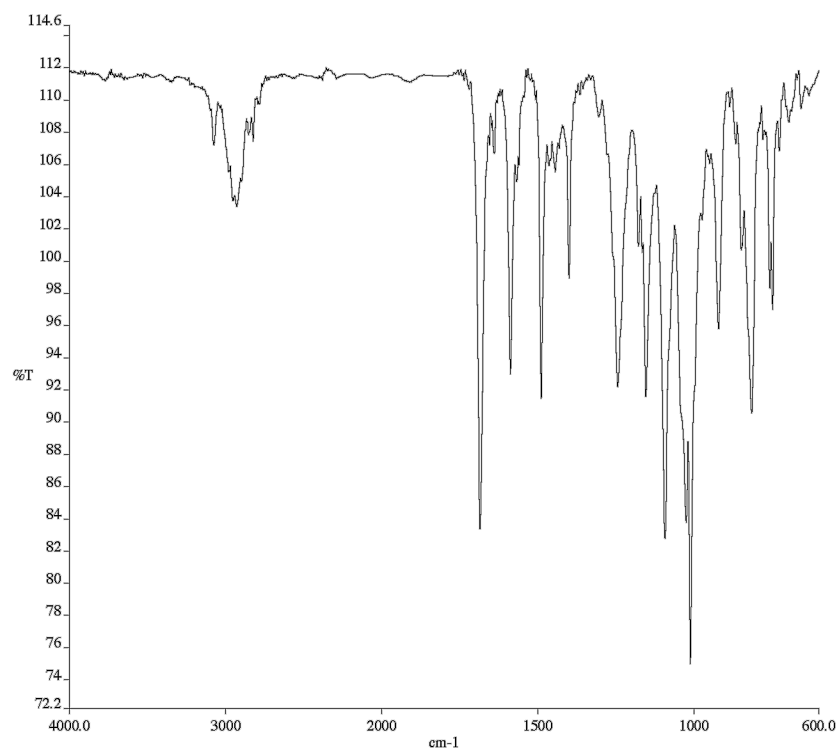
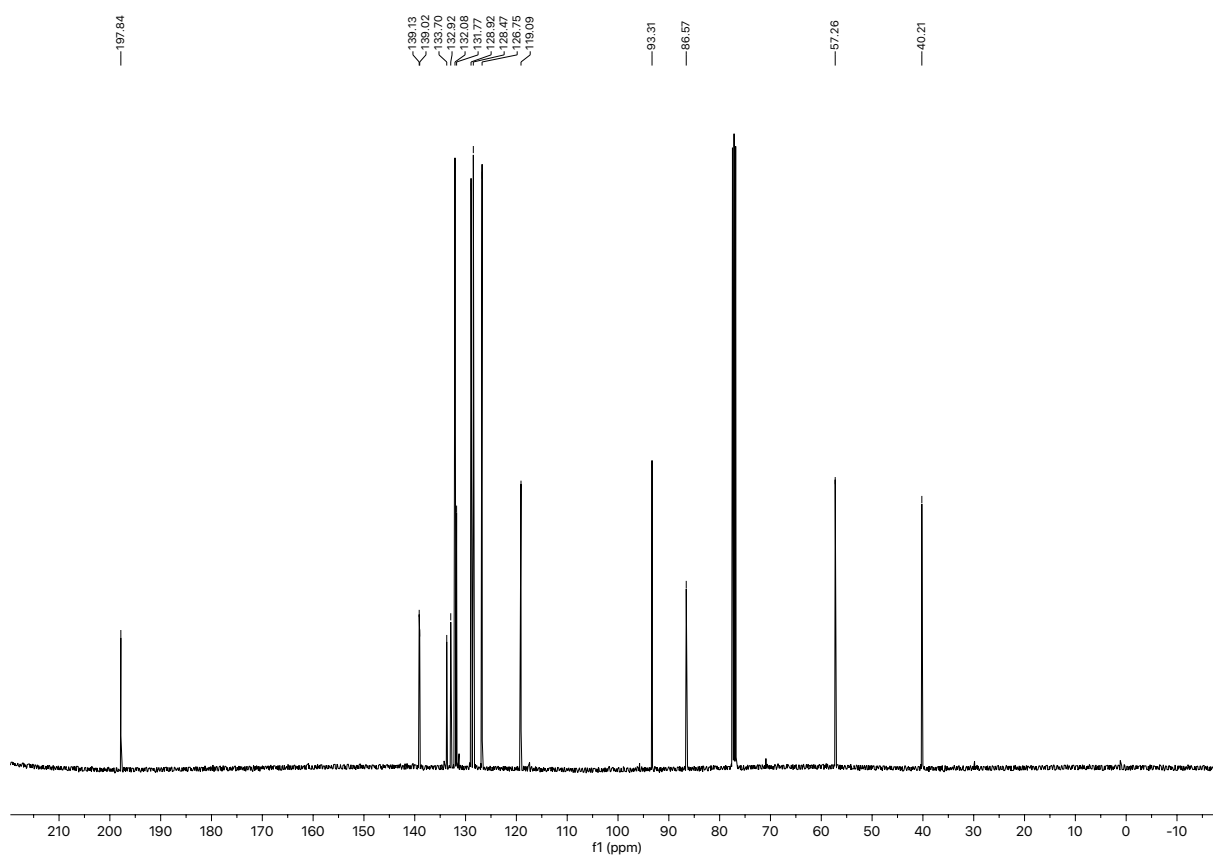
| Chemical Shift (ppm) | Integration |
|----------------------|-------------|
| 1.95 | 1.95 |
| 1.98 | 1.98 |
| 2.99 | 2.99 |
| 3.31 | 3.31 |
| 0.98 | 0.98 |
| 1.00 | 1.00 |
| 0.99 | 0.99 |
| 1.00 | 1.00 |
| 0.99 | 0.99 |
| 1.02 | 1.02 |
| 2.97 | 2.97 |
| 1.01 | 1.01 |

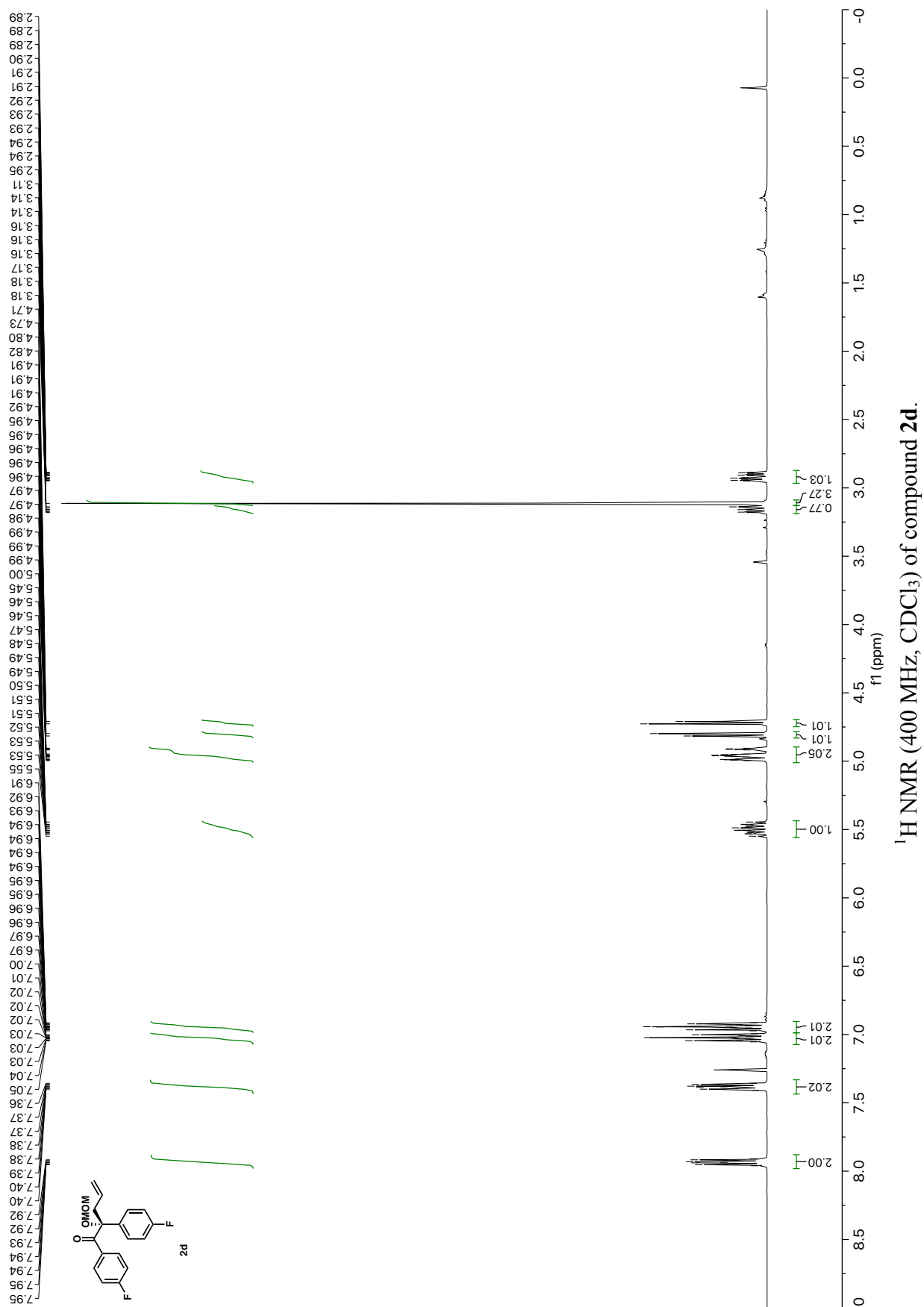
Infrared spectrum (Thin Film, NaCl) of compound **2a**.¹³C NMR (100 MHz, CDCl₃) of compound **2a**.

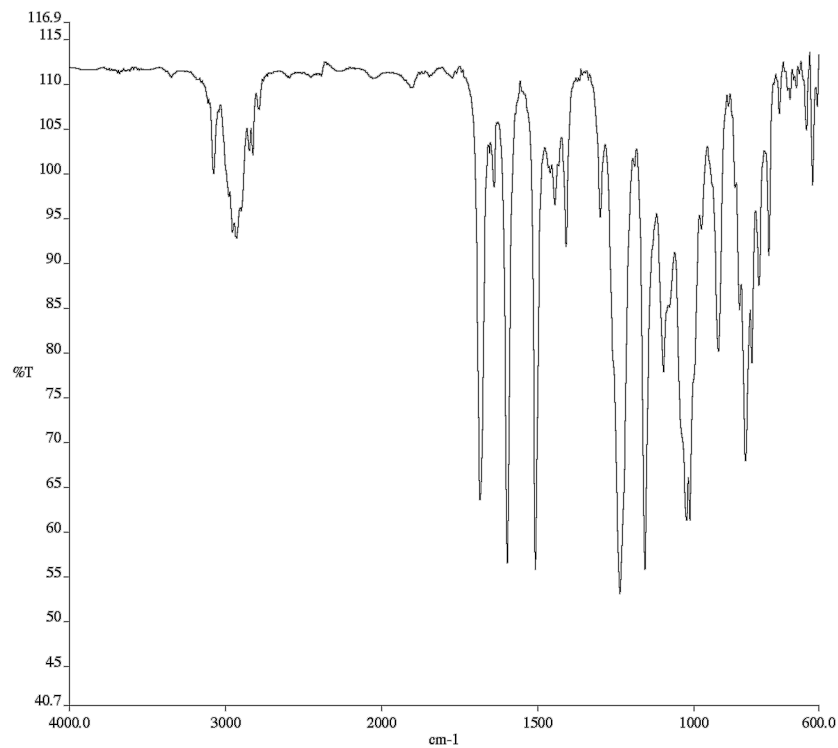
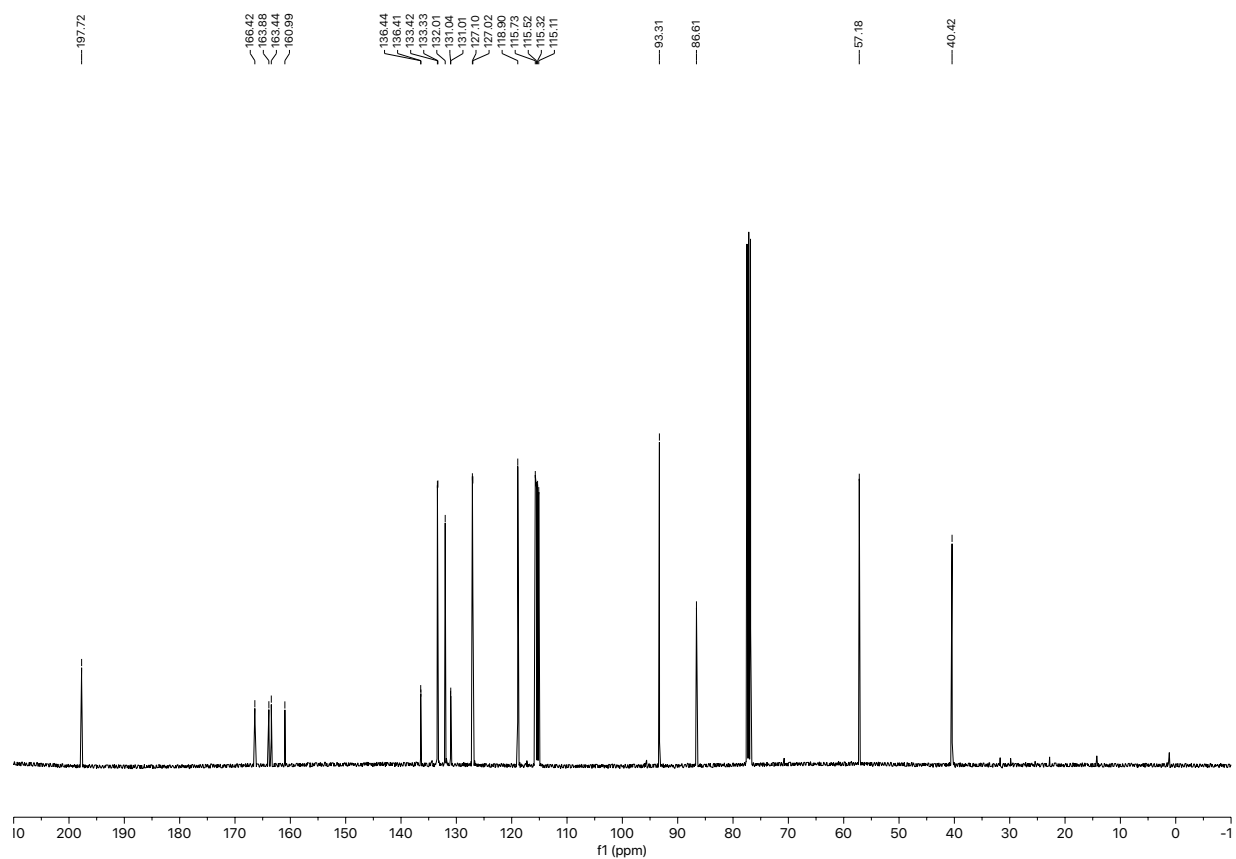


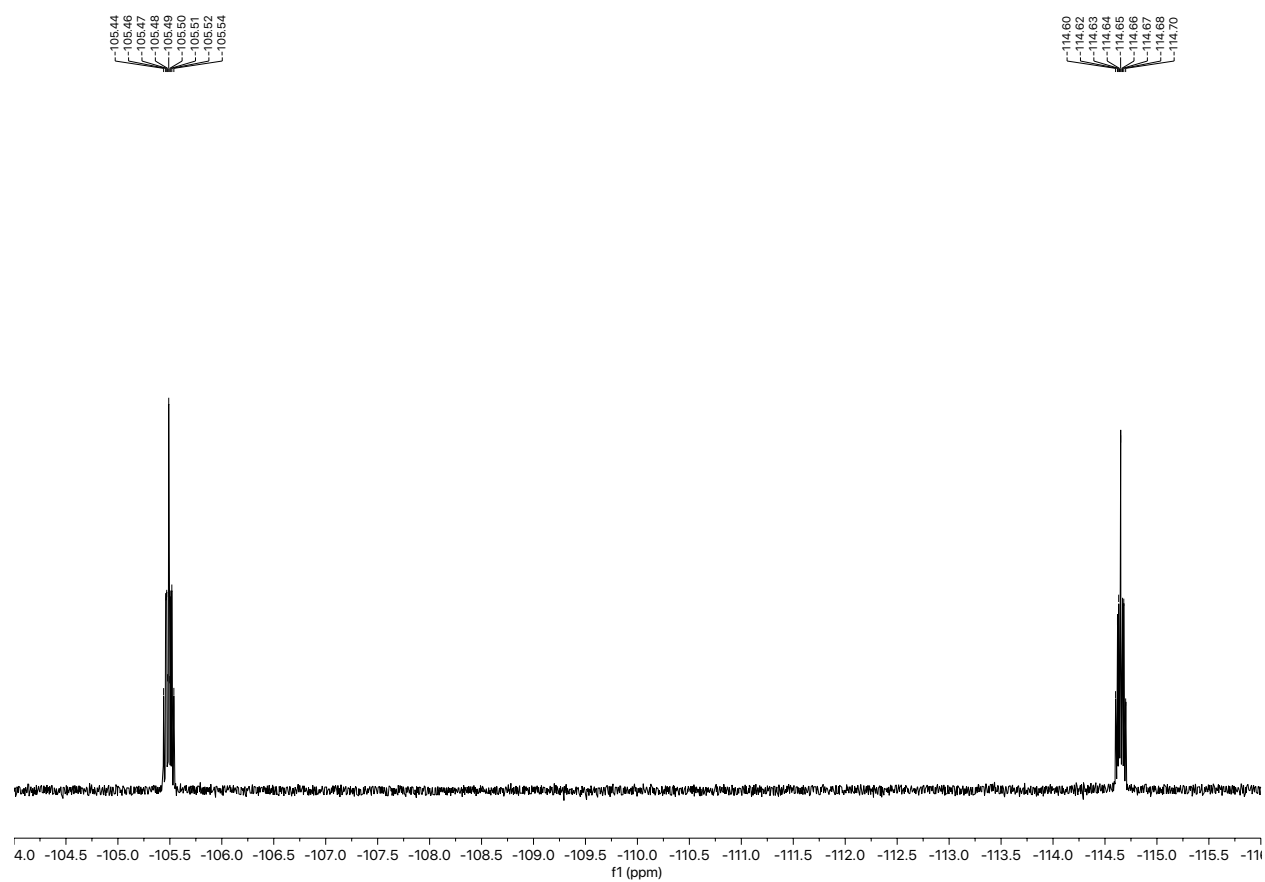
Infrared spectrum (Thin Film, NaCl) of compound **2b**.¹³C NMR (100 MHz, CDCl₃) of compound **2b**.



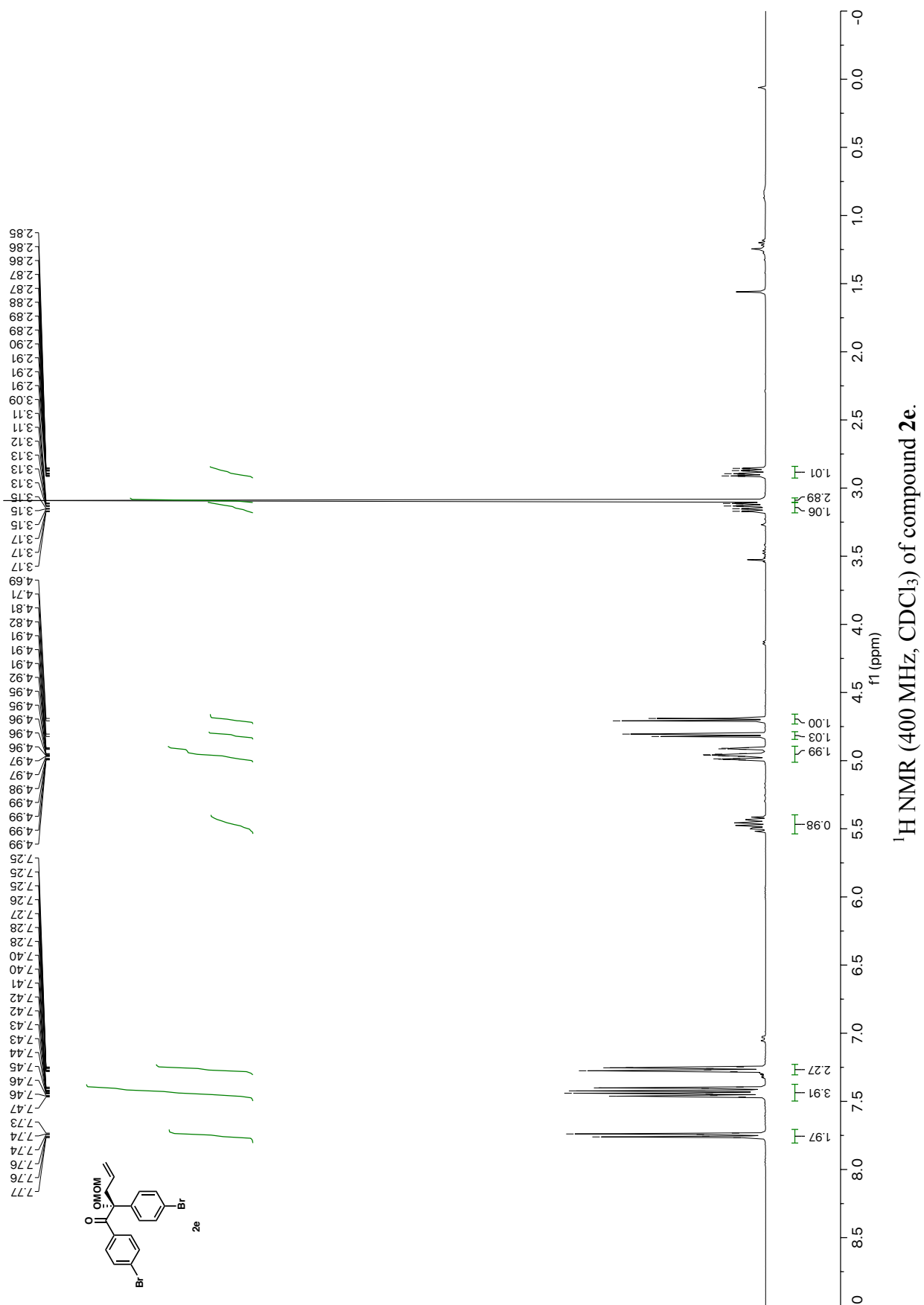
Infrared spectrum (Thin Film, NaCl) of compound **2c**.¹³C NMR (100 MHz, CDCl₃) of compound **2c**.

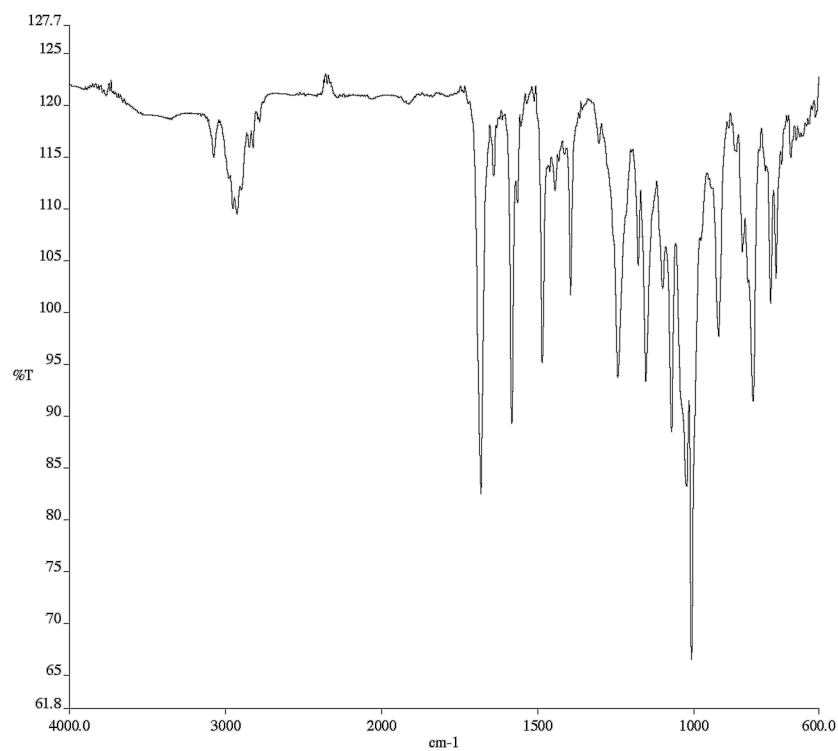
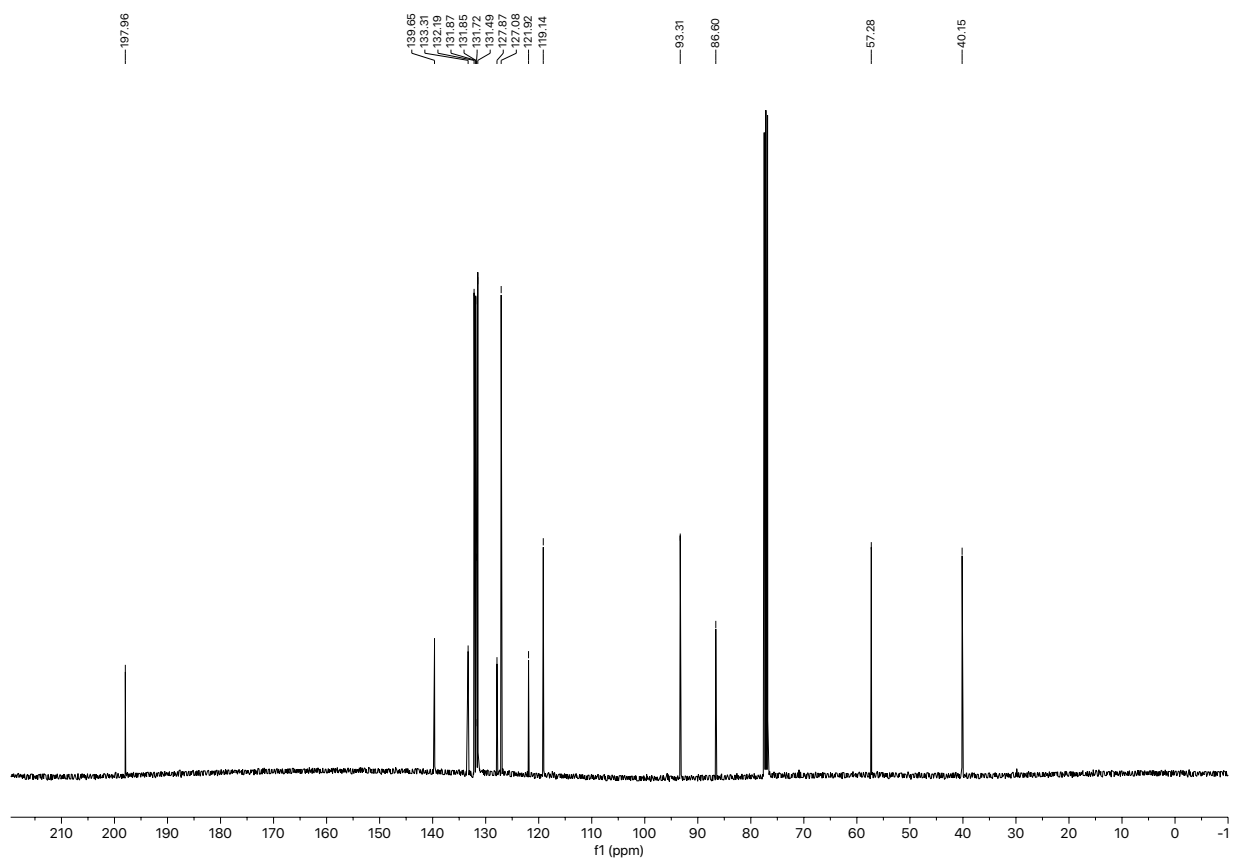


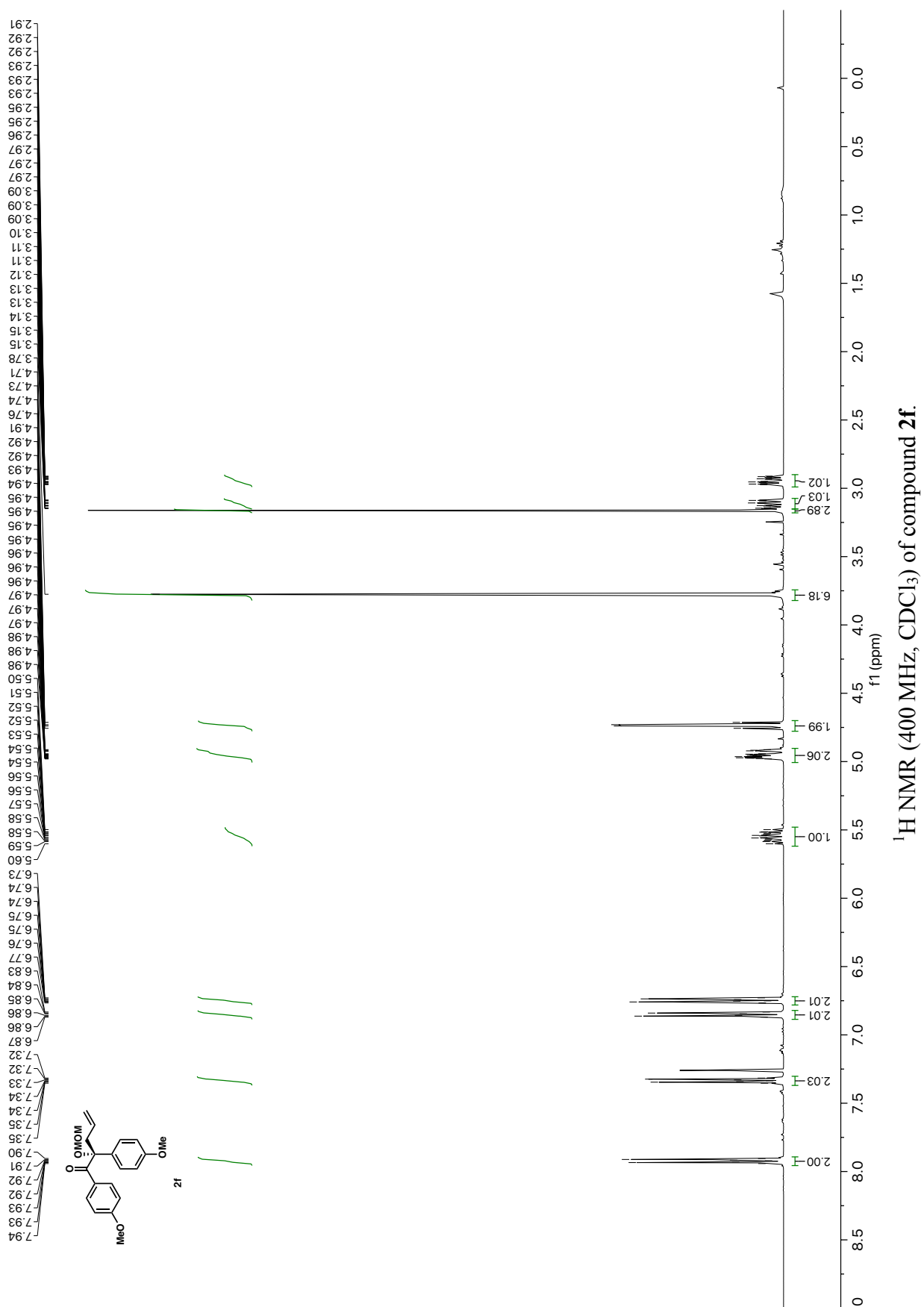
Infrared spectrum (Thin Film, NaCl) of compound **2d**.¹³C NMR (100 MHz, CDCl₃) of compound **2d**.

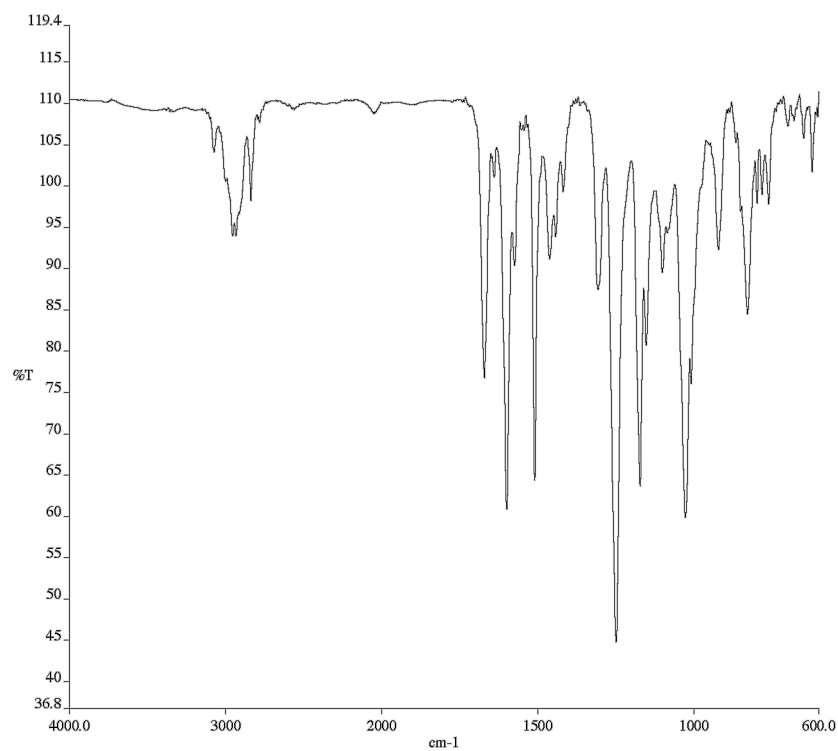
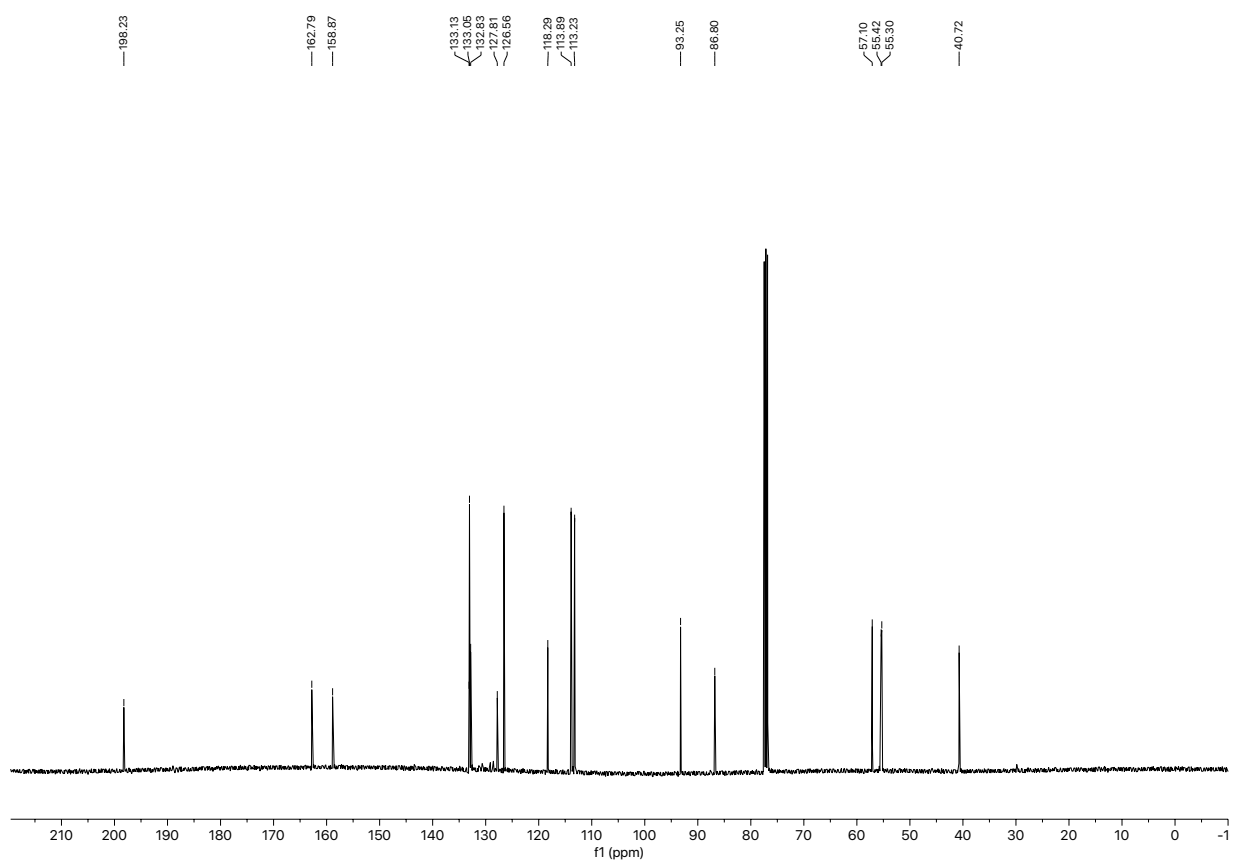


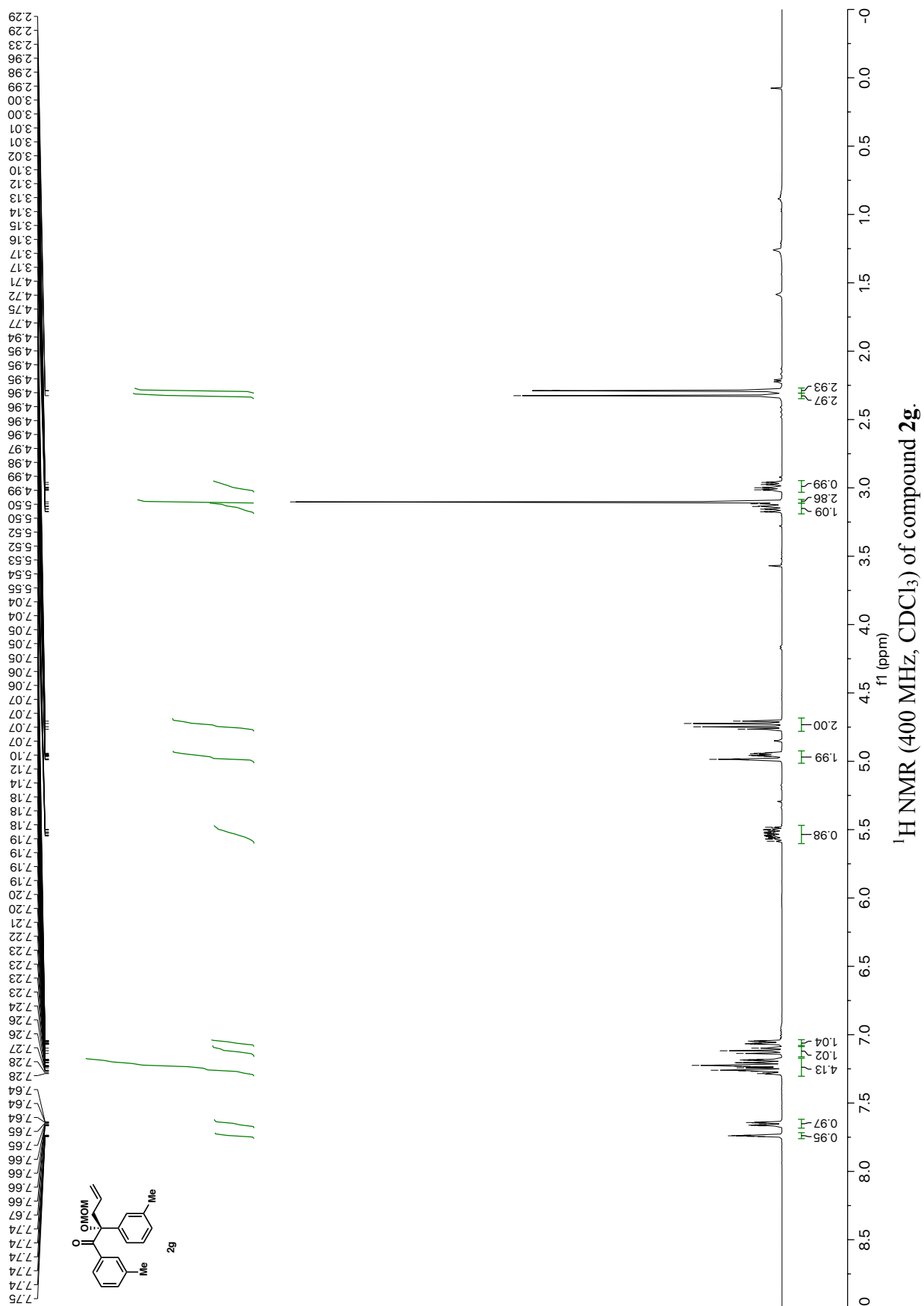
^{19}F NMR (282 MHz, CDCl_3) of compound **2d**.

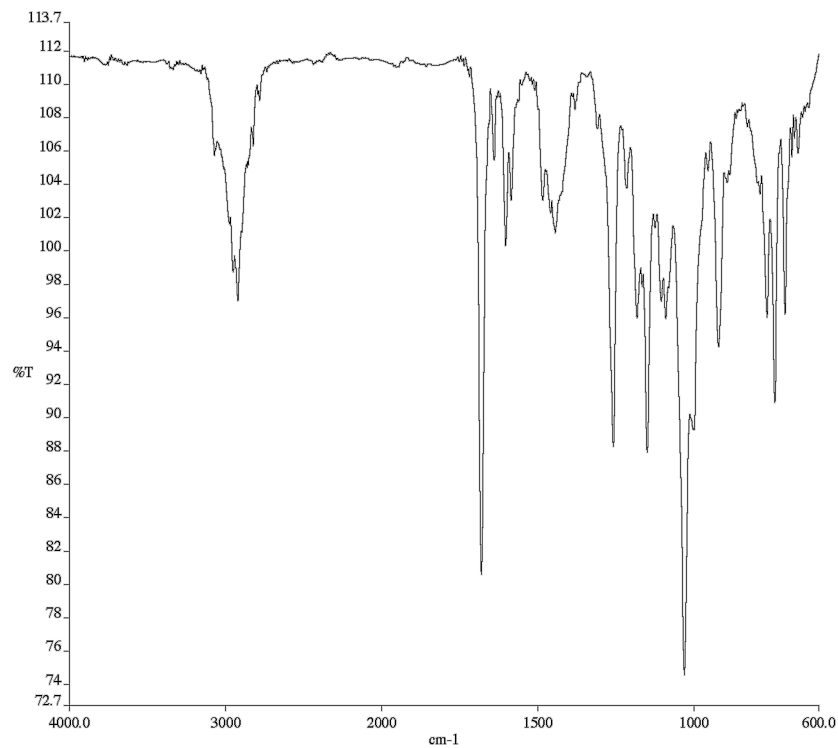
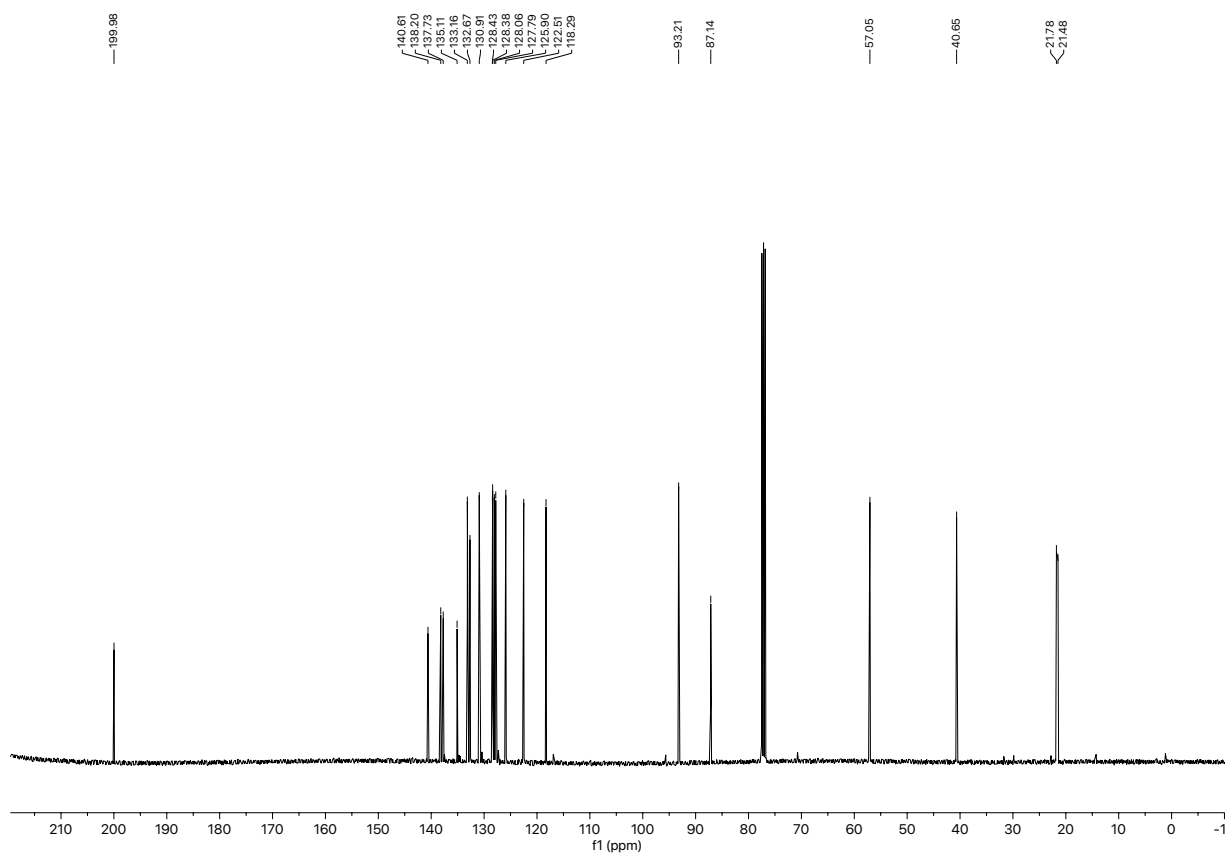


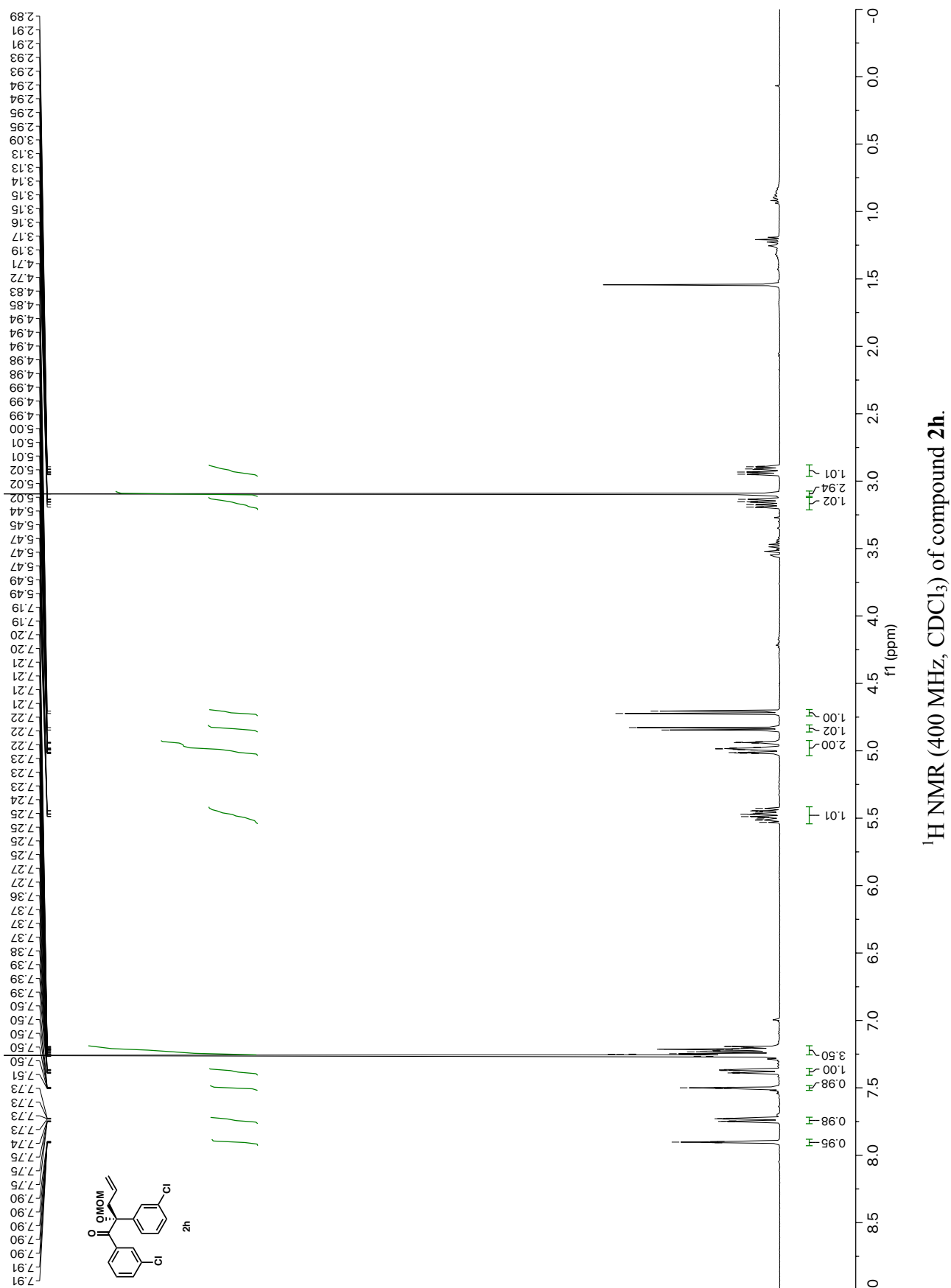
Infrared spectrum (Thin Film, NaCl) of compound **2e**.¹³C NMR (100 MHz, CDCl₃) of compound **2e**.

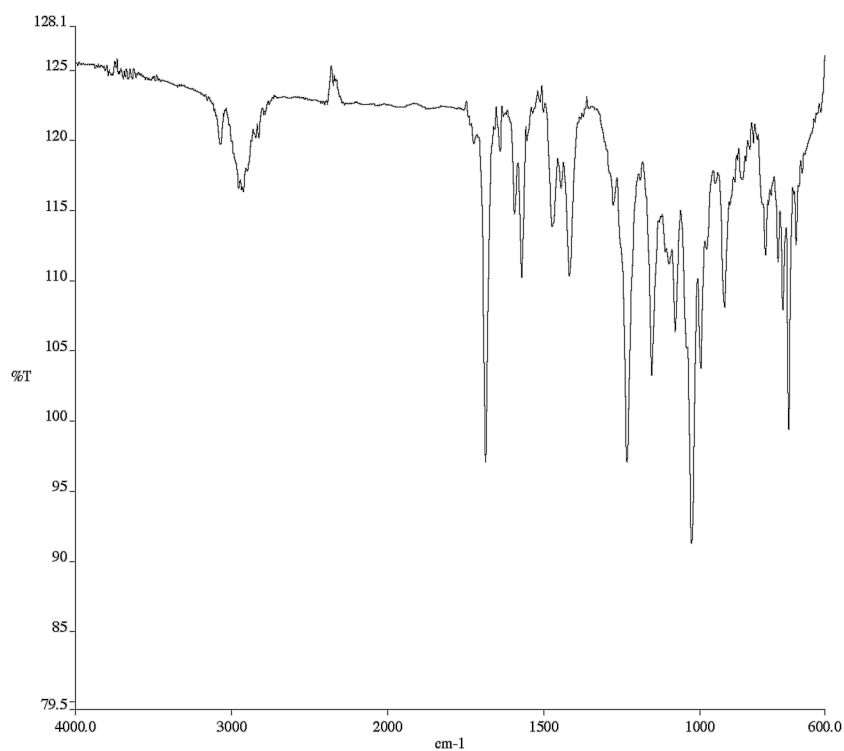
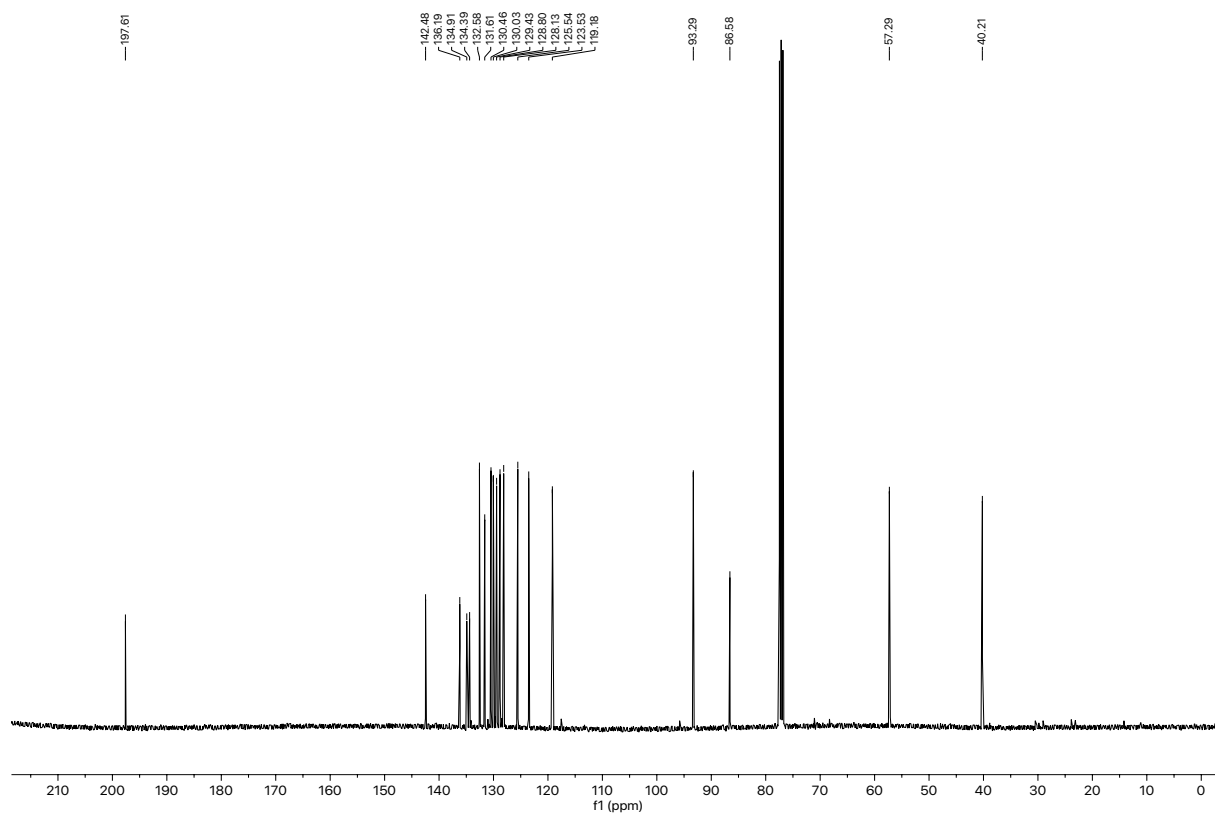


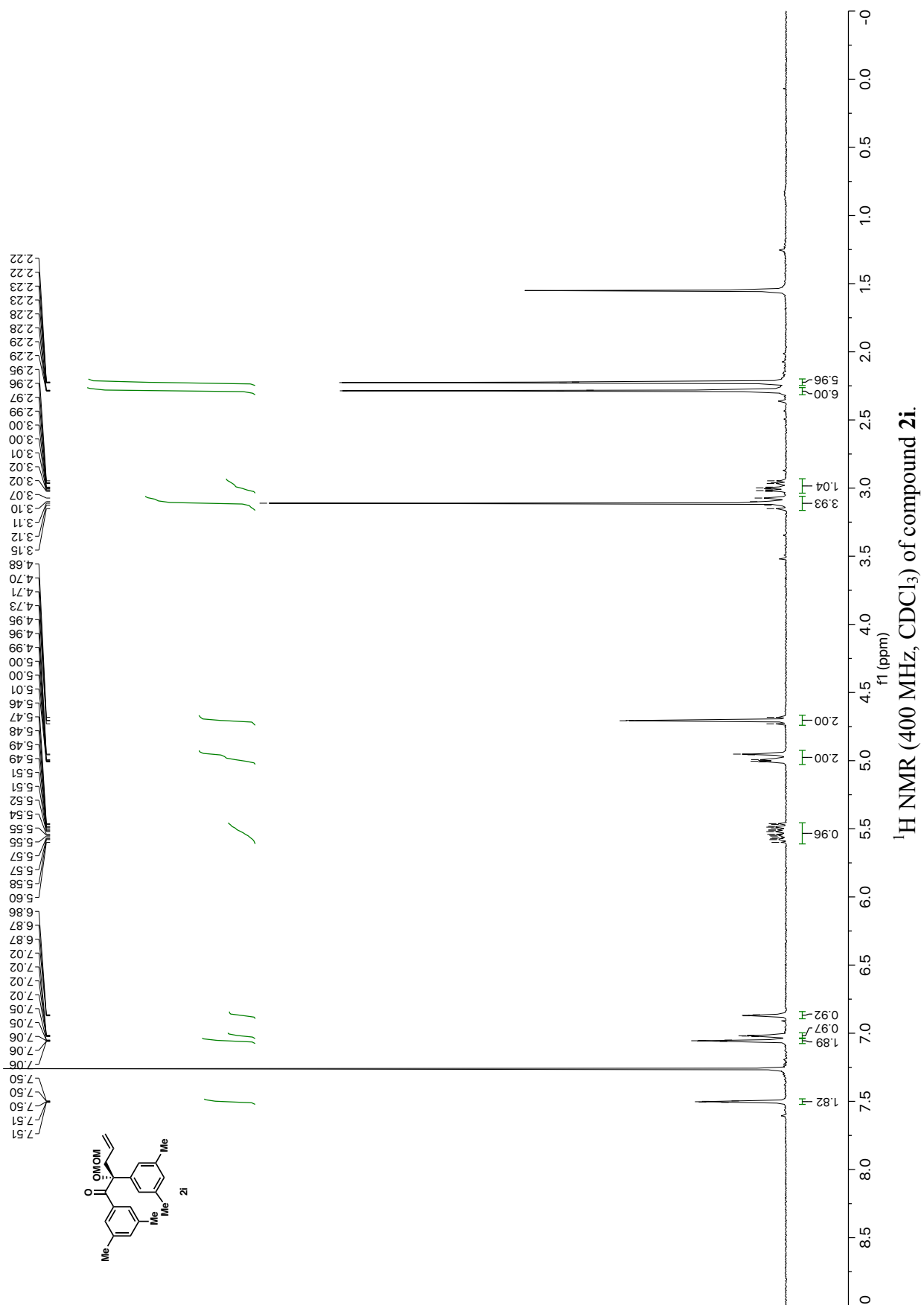
Infrared spectrum (Thin Film, NaCl) of compound **2f**.¹³C NMR (100 MHz, CDCl₃) of compound **2f**.

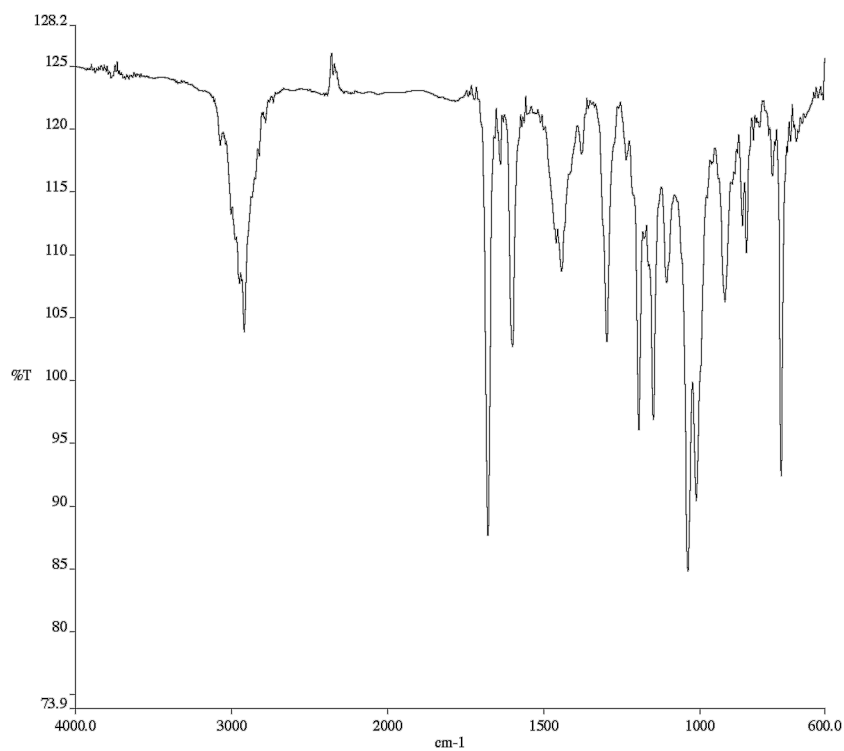
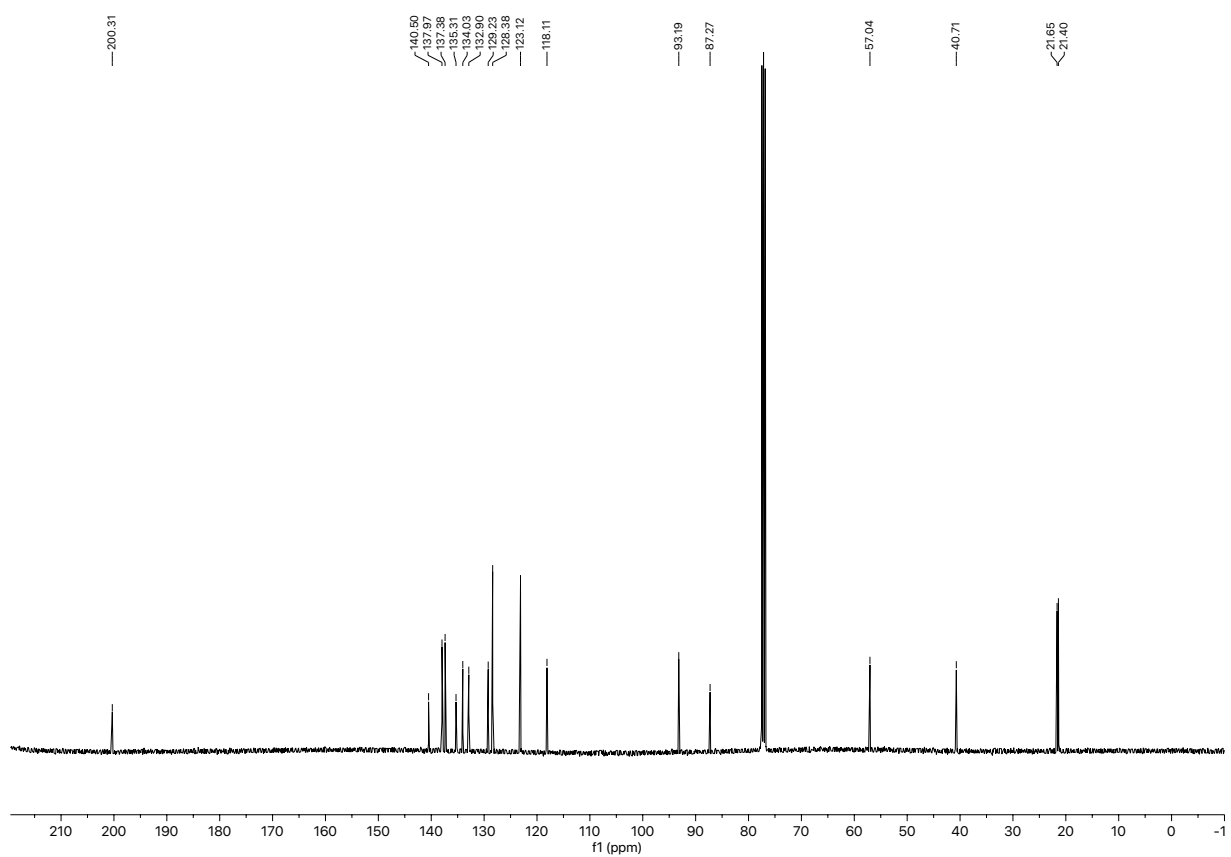


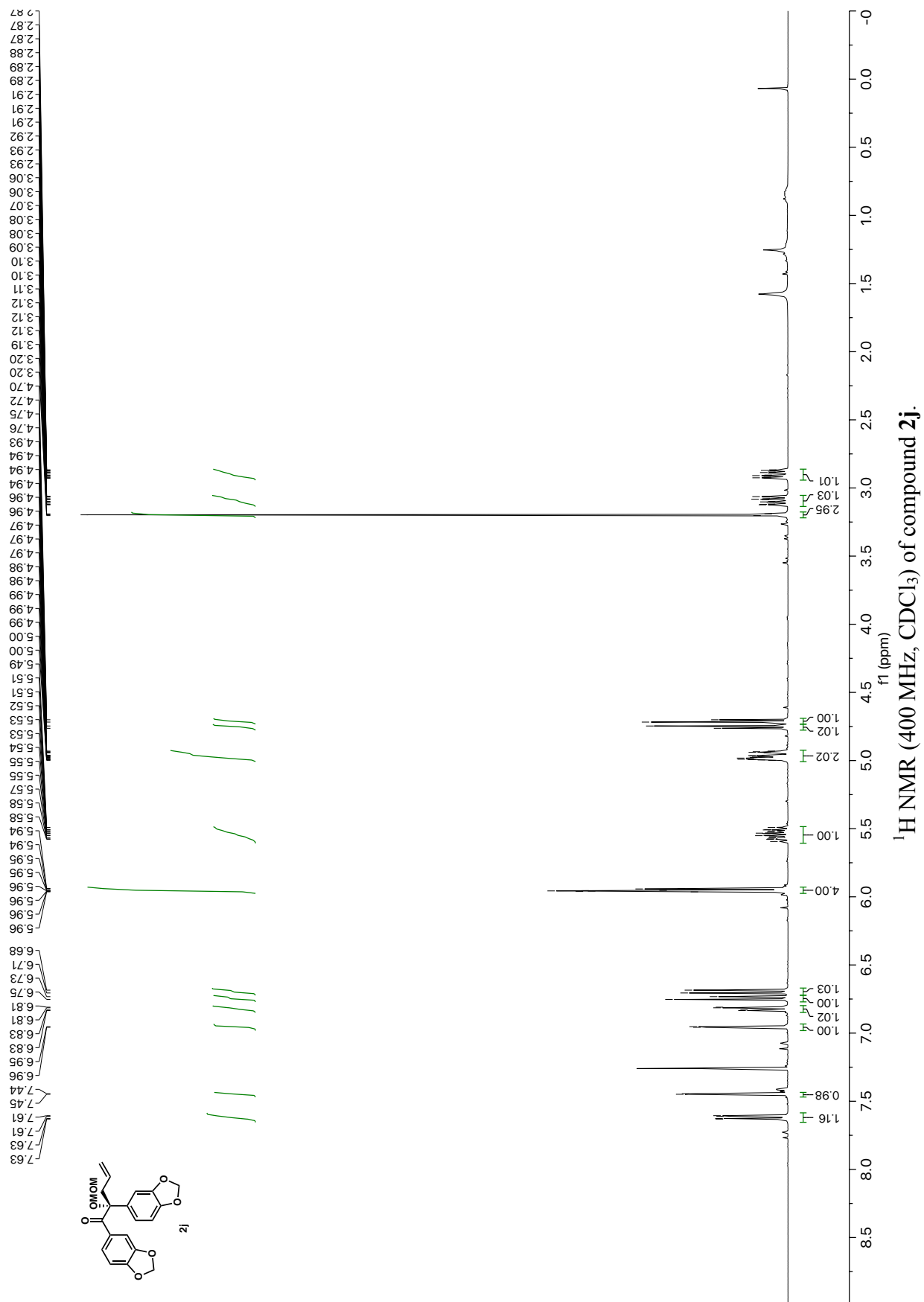
Infrared spectrum (Thin Film, NaCl) of compound **2g**.¹³C NMR (100 MHz, CDCl₃) of compound **2g**.

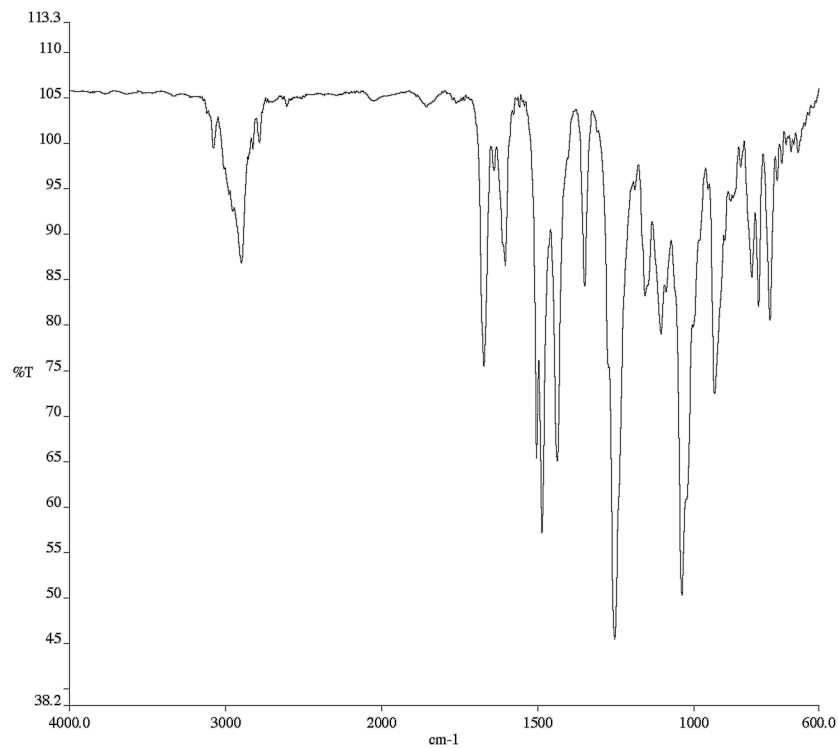
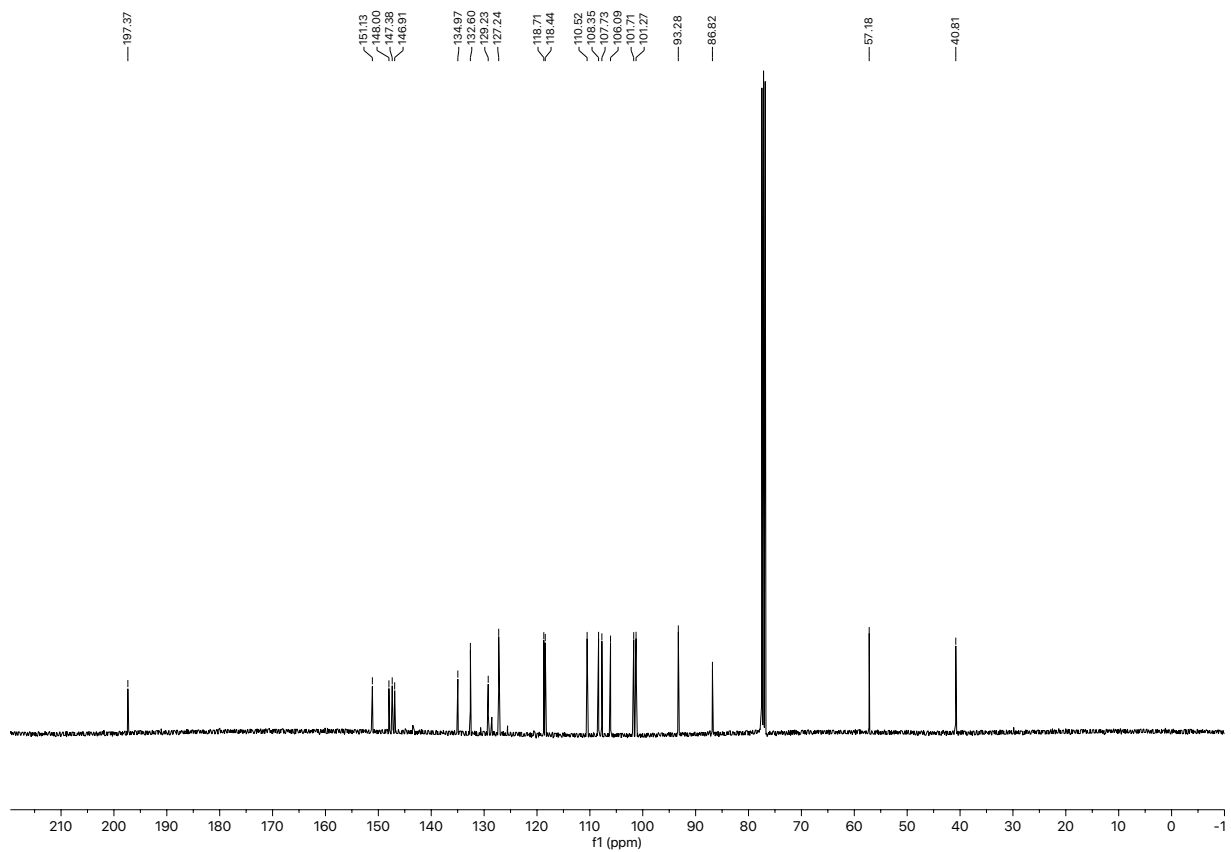


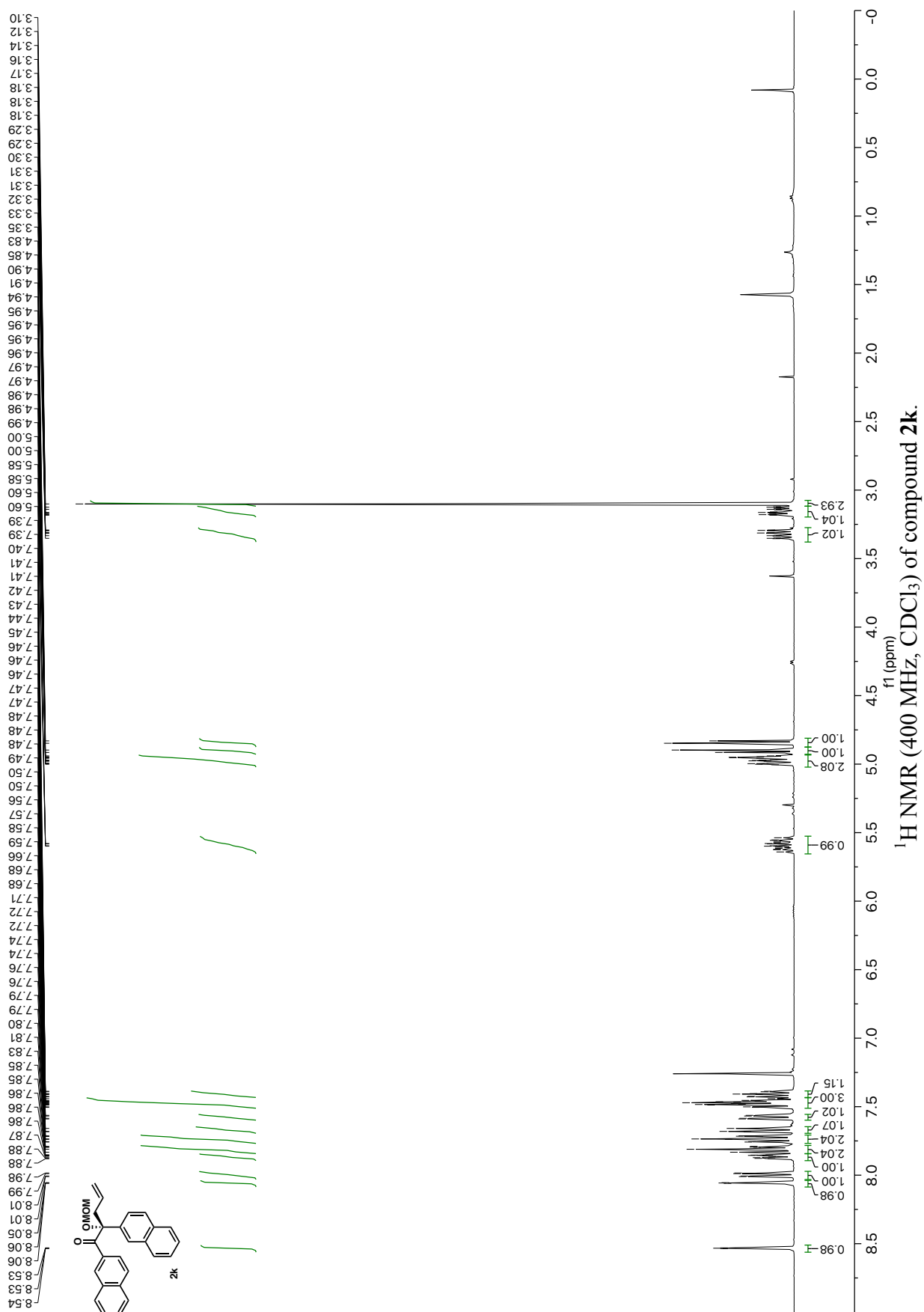
Infrared spectrum (Thin Film, NaCl) of compound **2h**.¹³C NMR (100 MHz, CDCl₃) of compound **2h**.

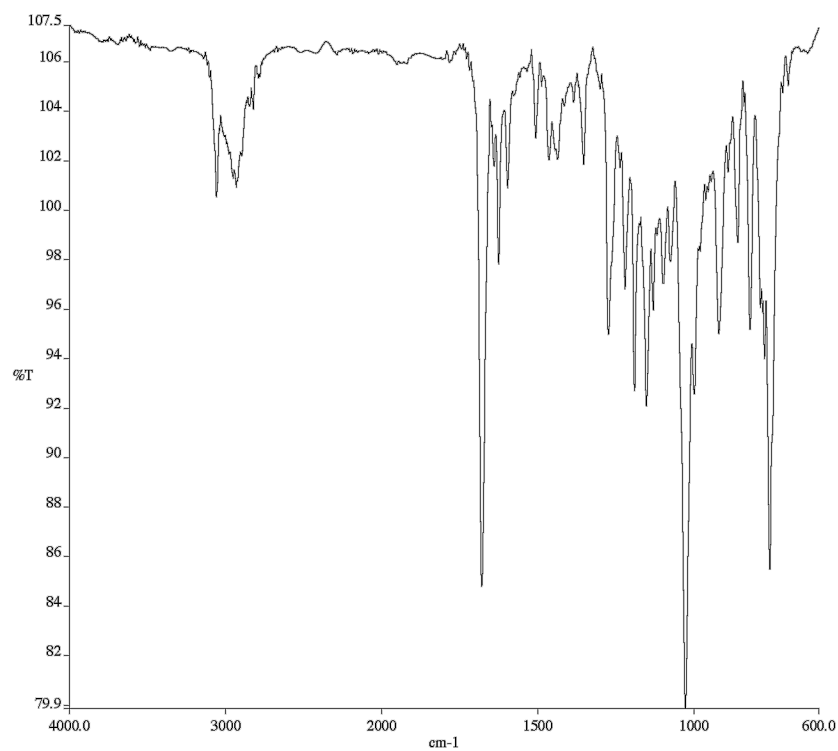
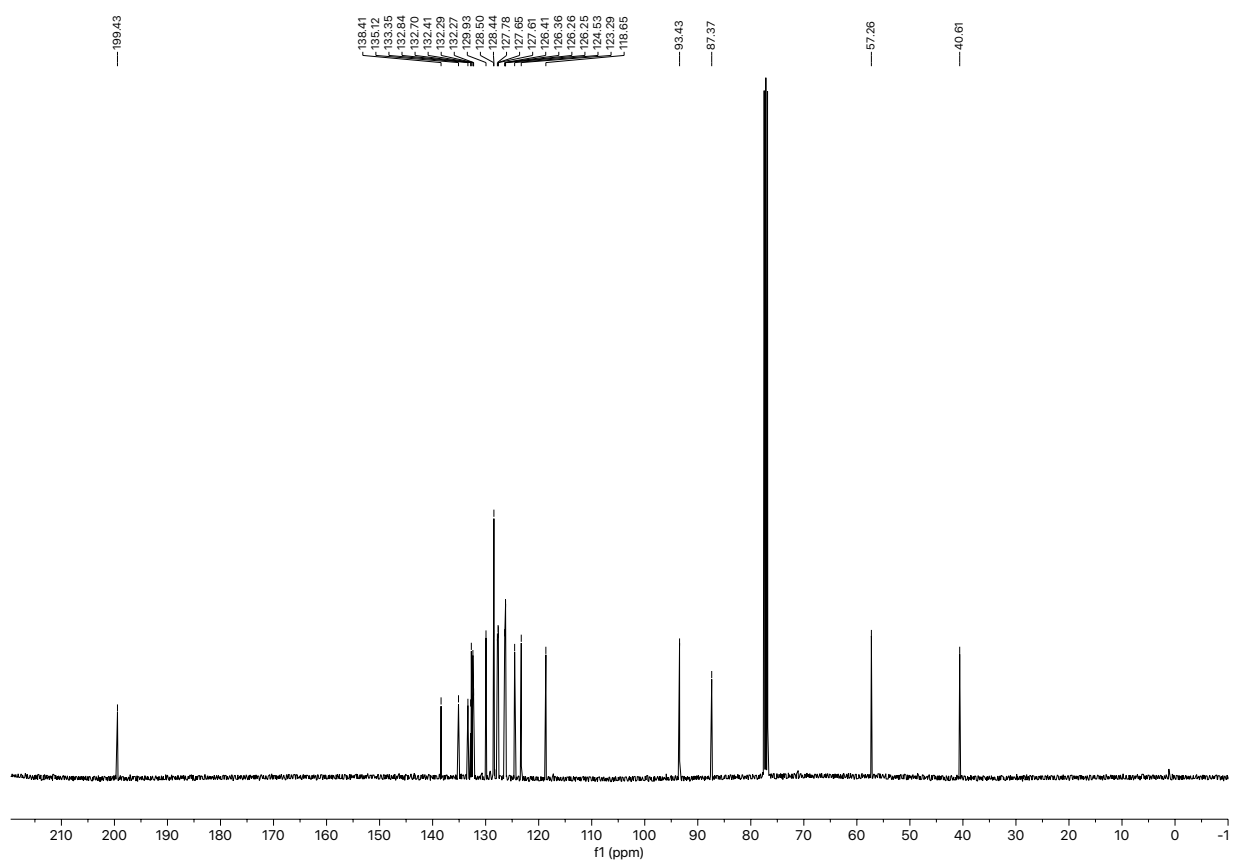


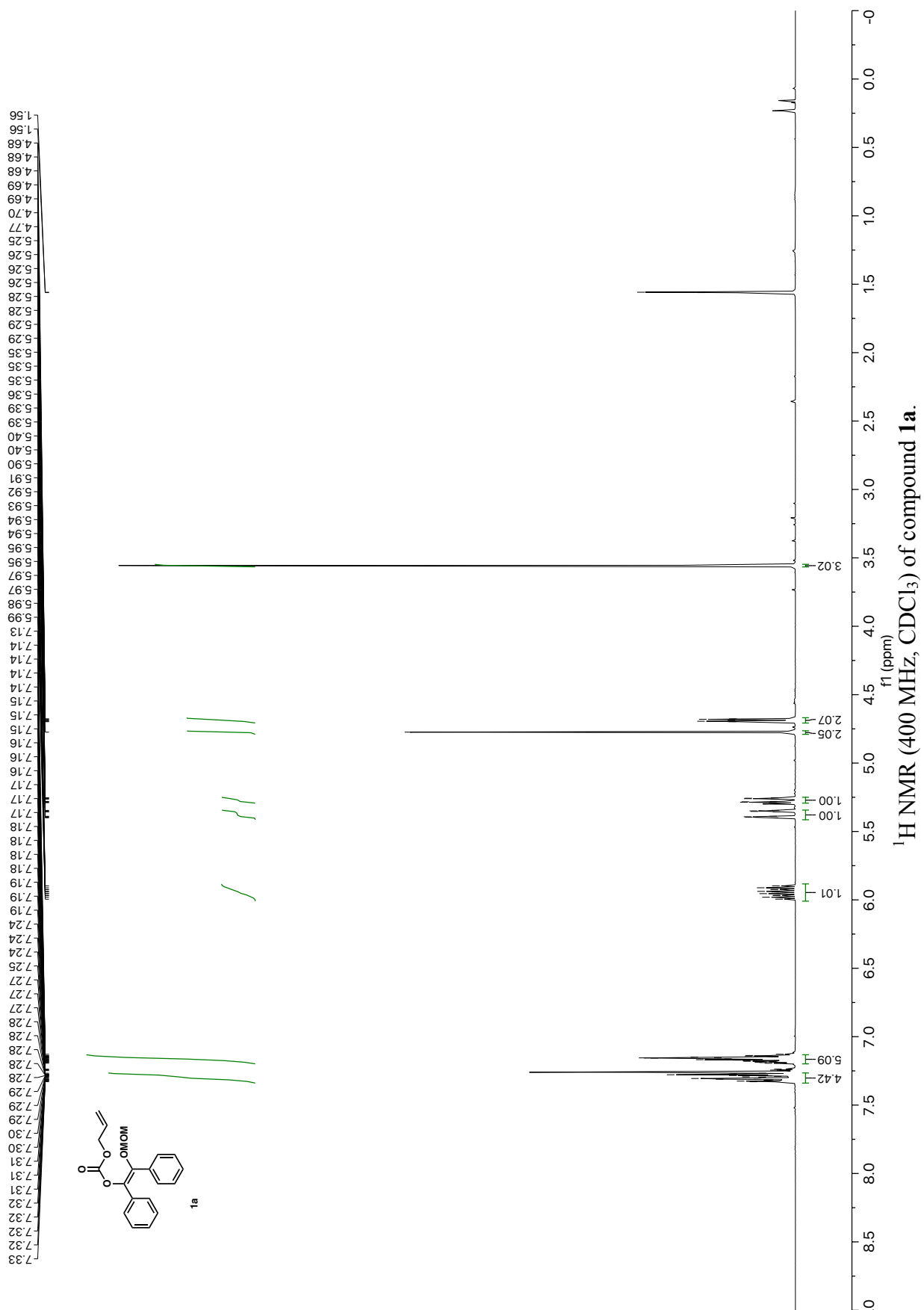
Infrared spectrum (Thin Film, NaCl) of compound **2i**.¹³C NMR (100 MHz, CDCl₃) of compound **2i**.

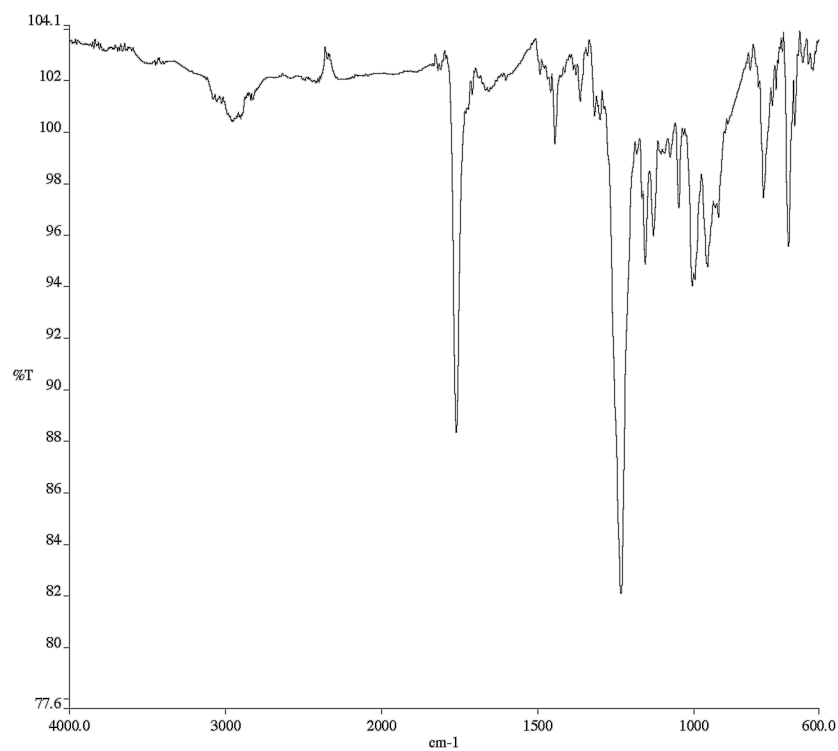
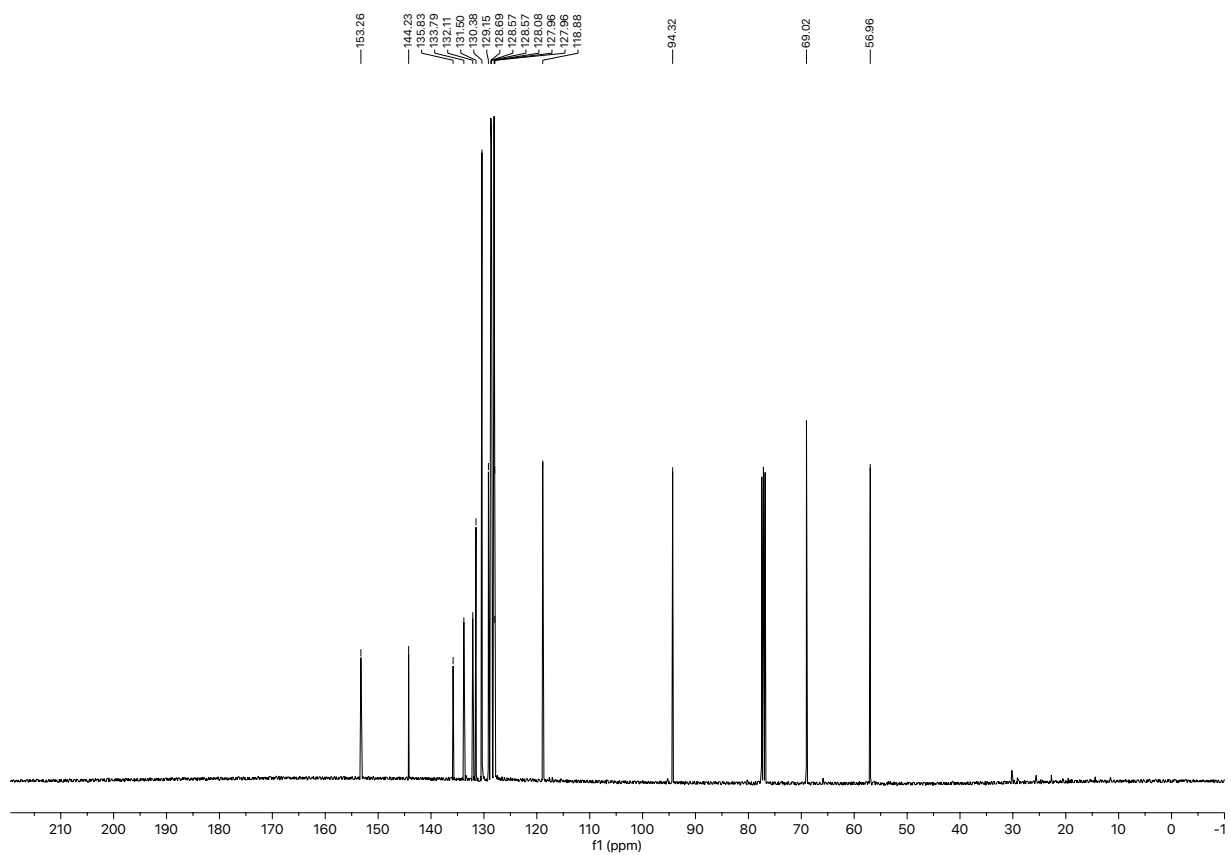


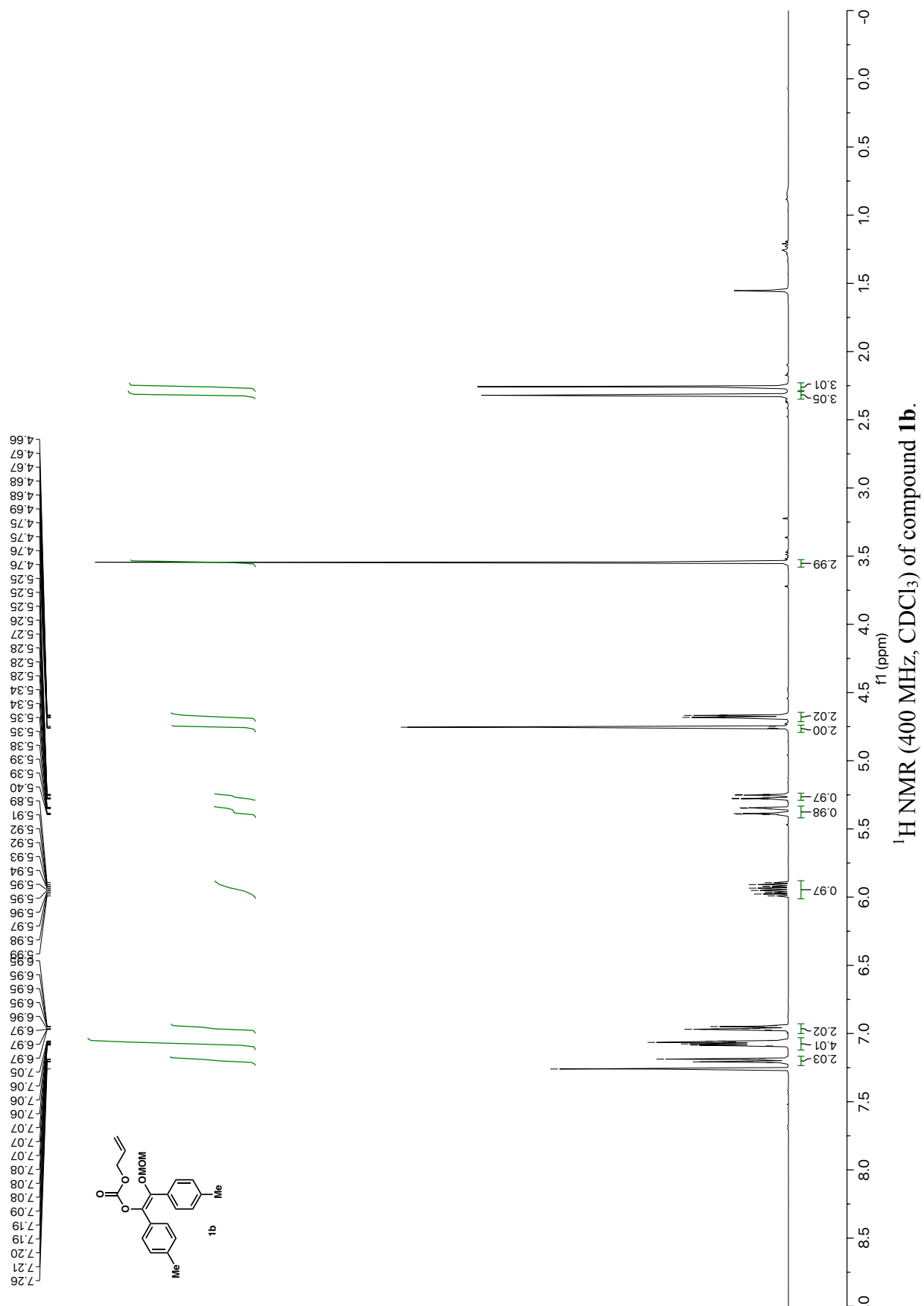
Infrared spectrum (Thin Film, NaCl) of compound **2j**.¹³C NMR (100 MHz, CDCl₃) of compound **2j**.

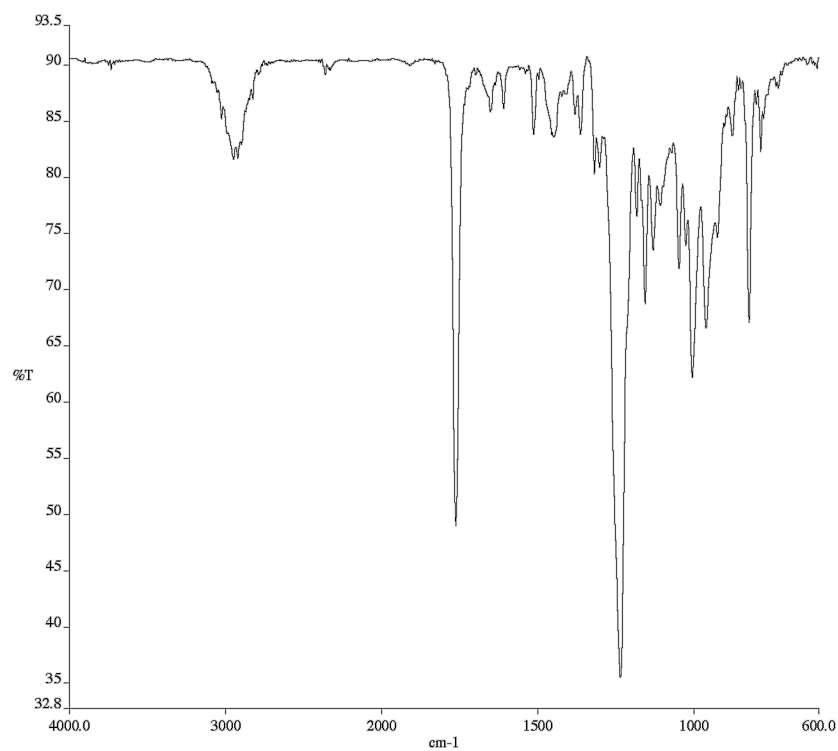
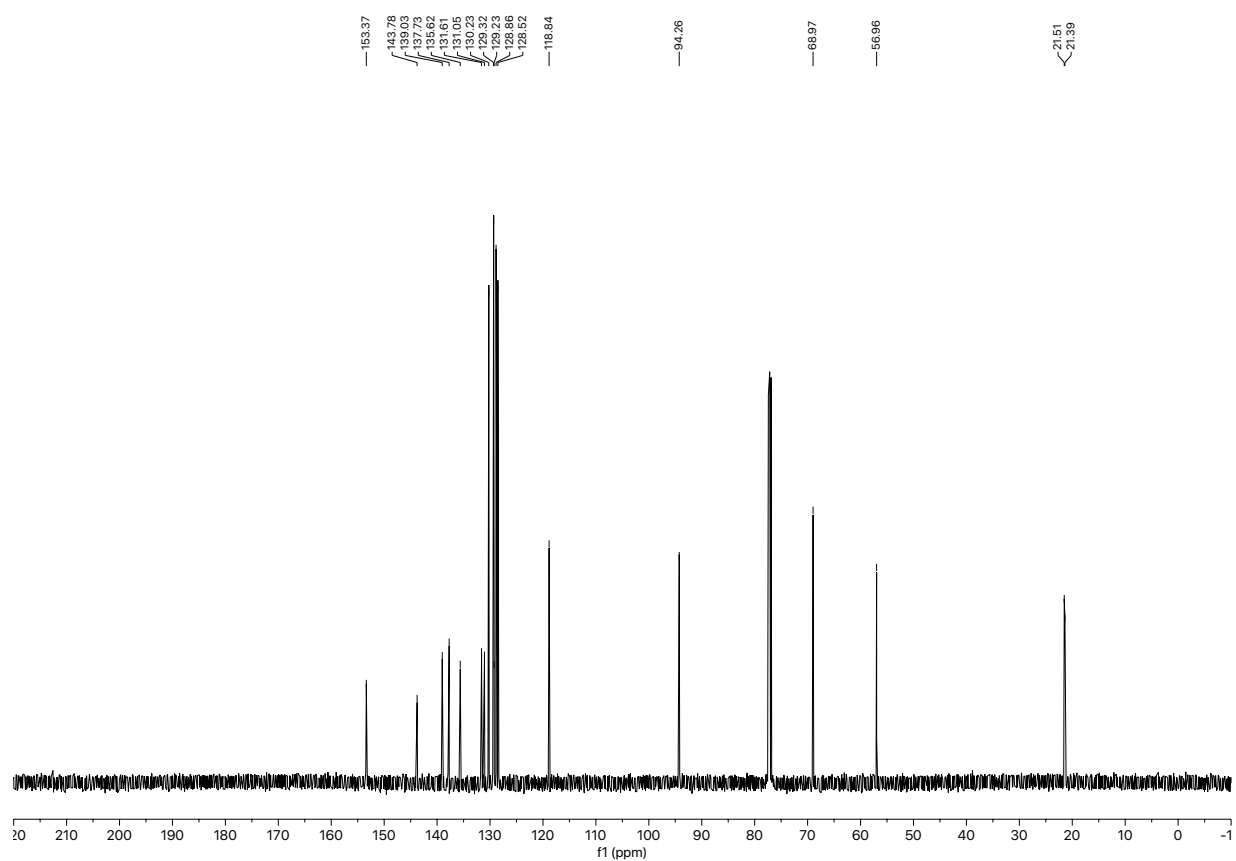


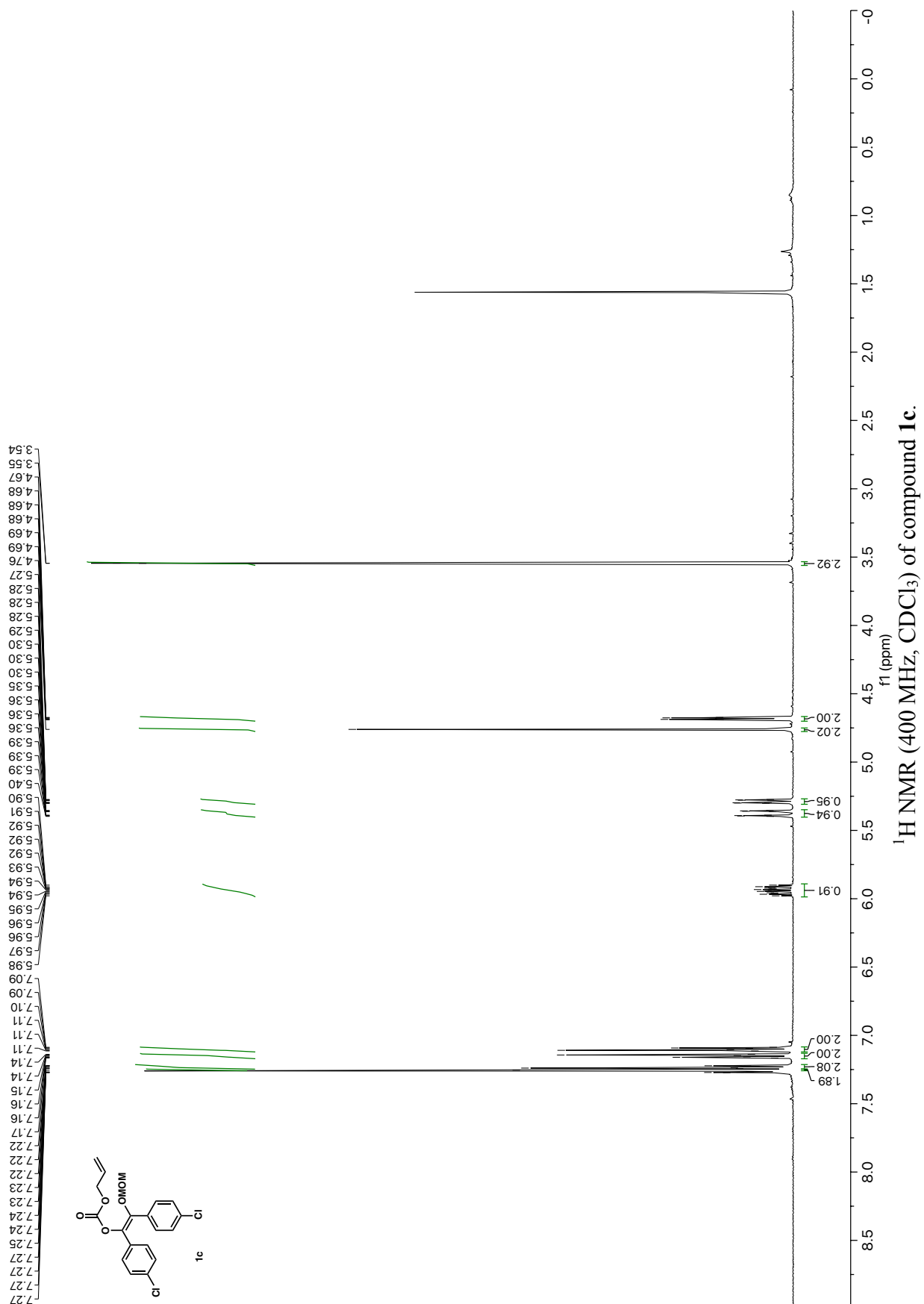
Infrared spectrum (Thin Film, NaCl) of compound **2k**.¹³C NMR (100 MHz, CDCl₃) of compound **2k**.

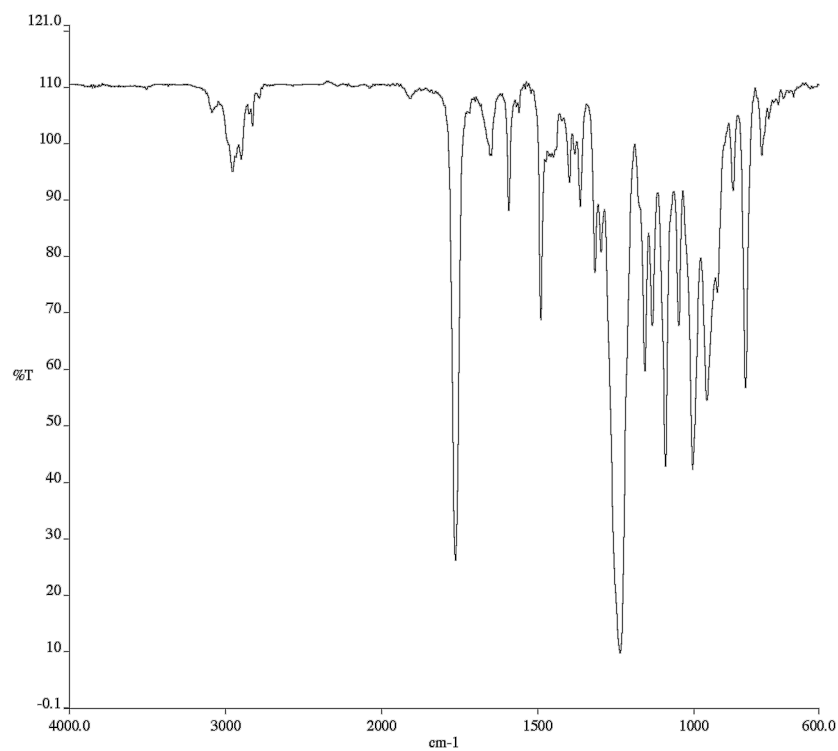
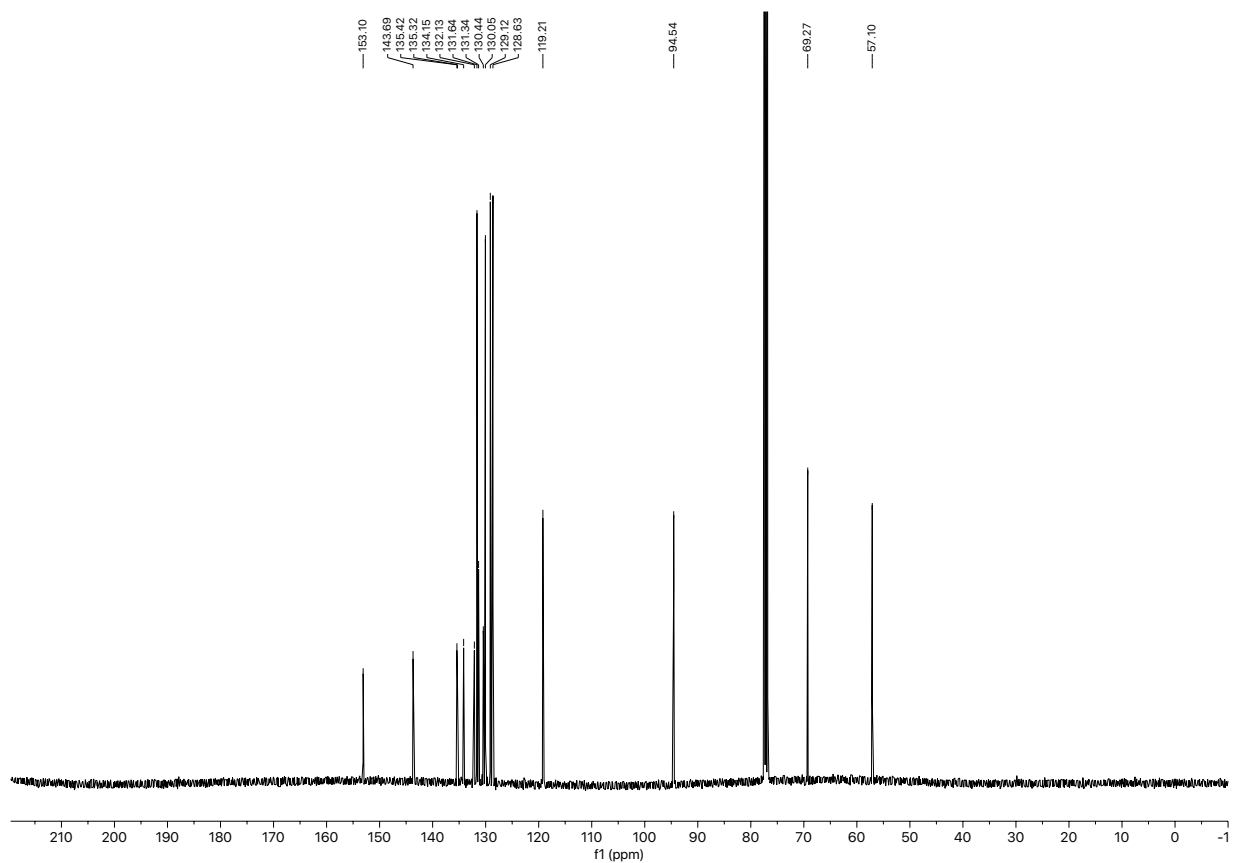


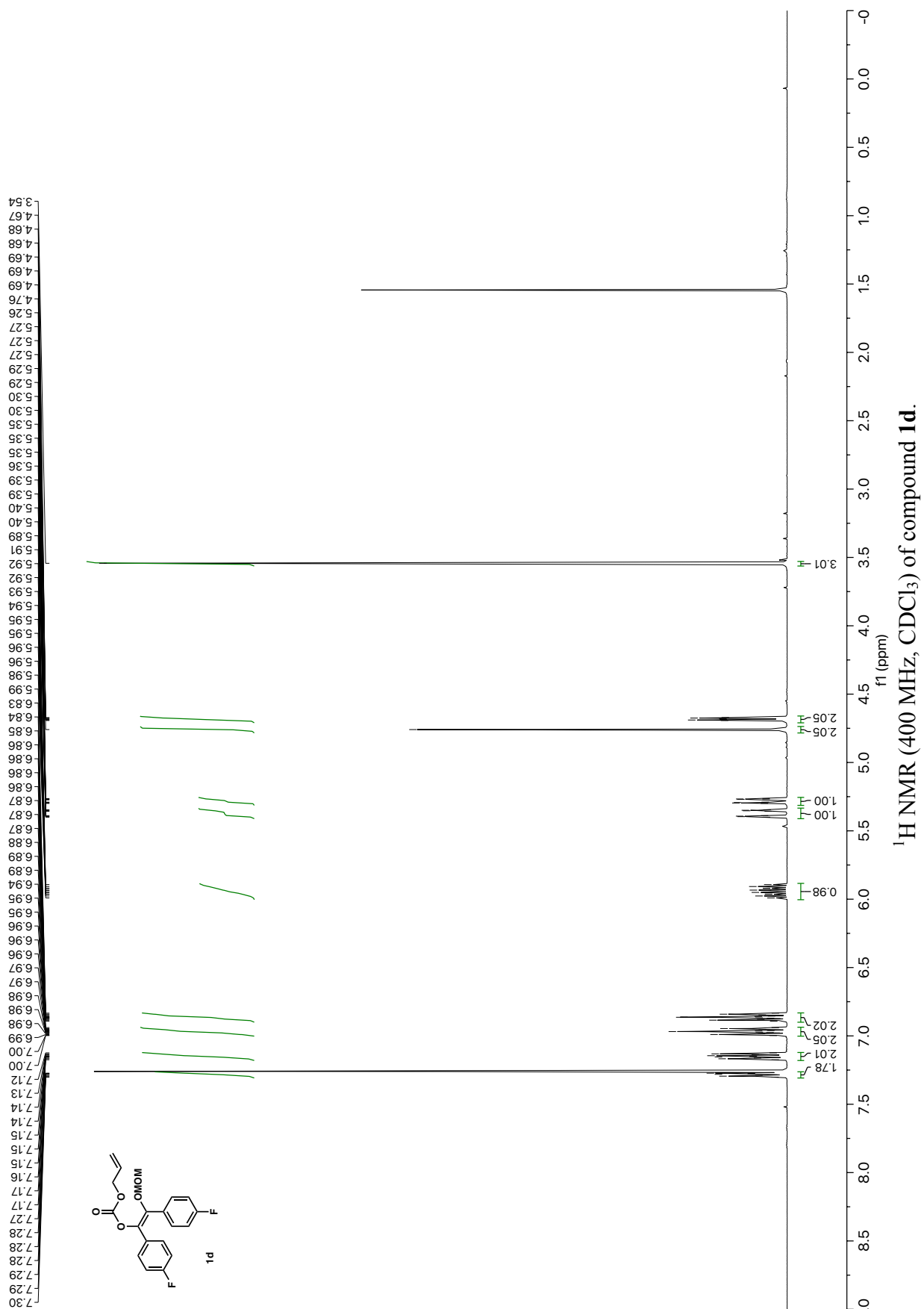
Infrared spectrum (Thin Film, NaCl) of compound **1a**.¹³C NMR (100 MHz, CDCl₃) of compound **1a**.

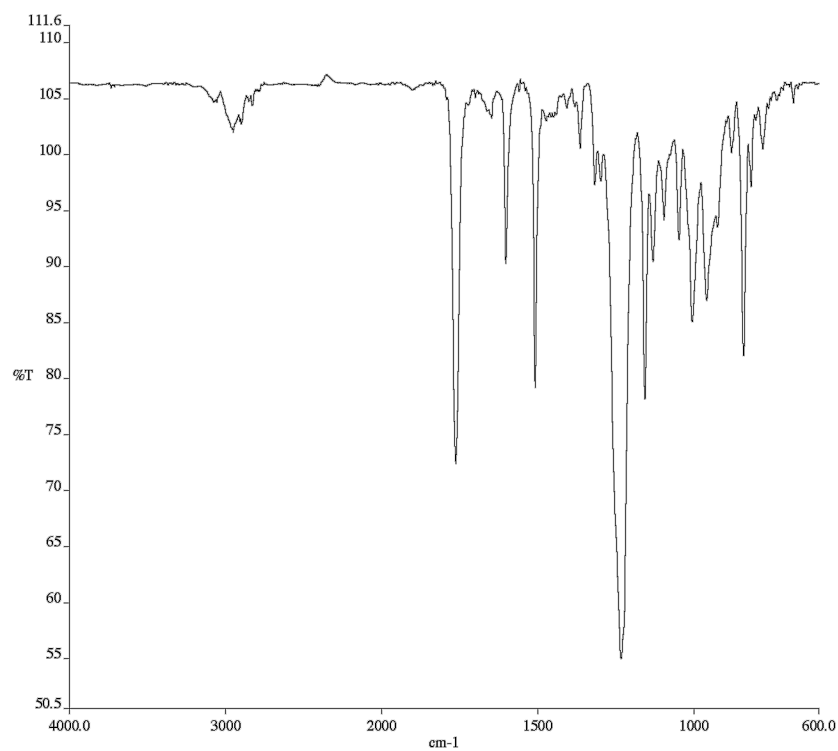
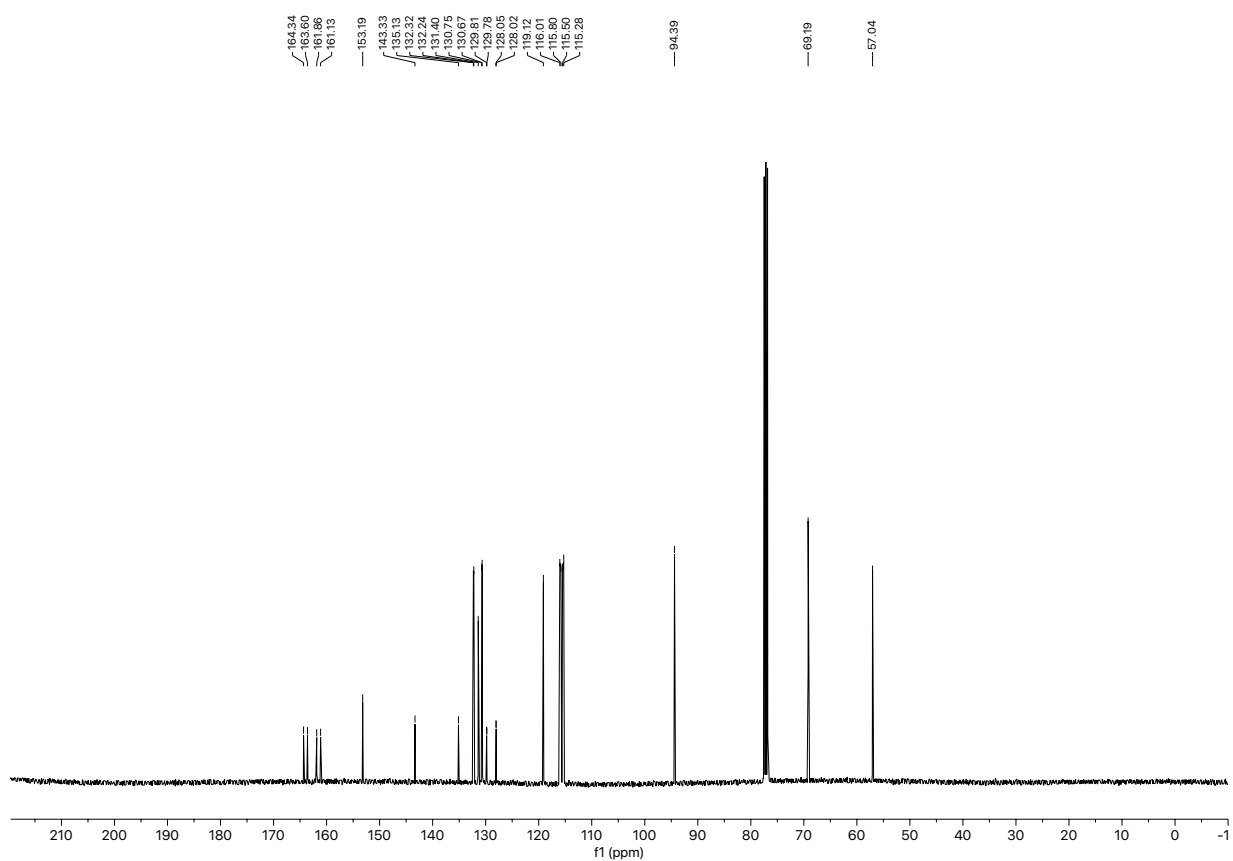


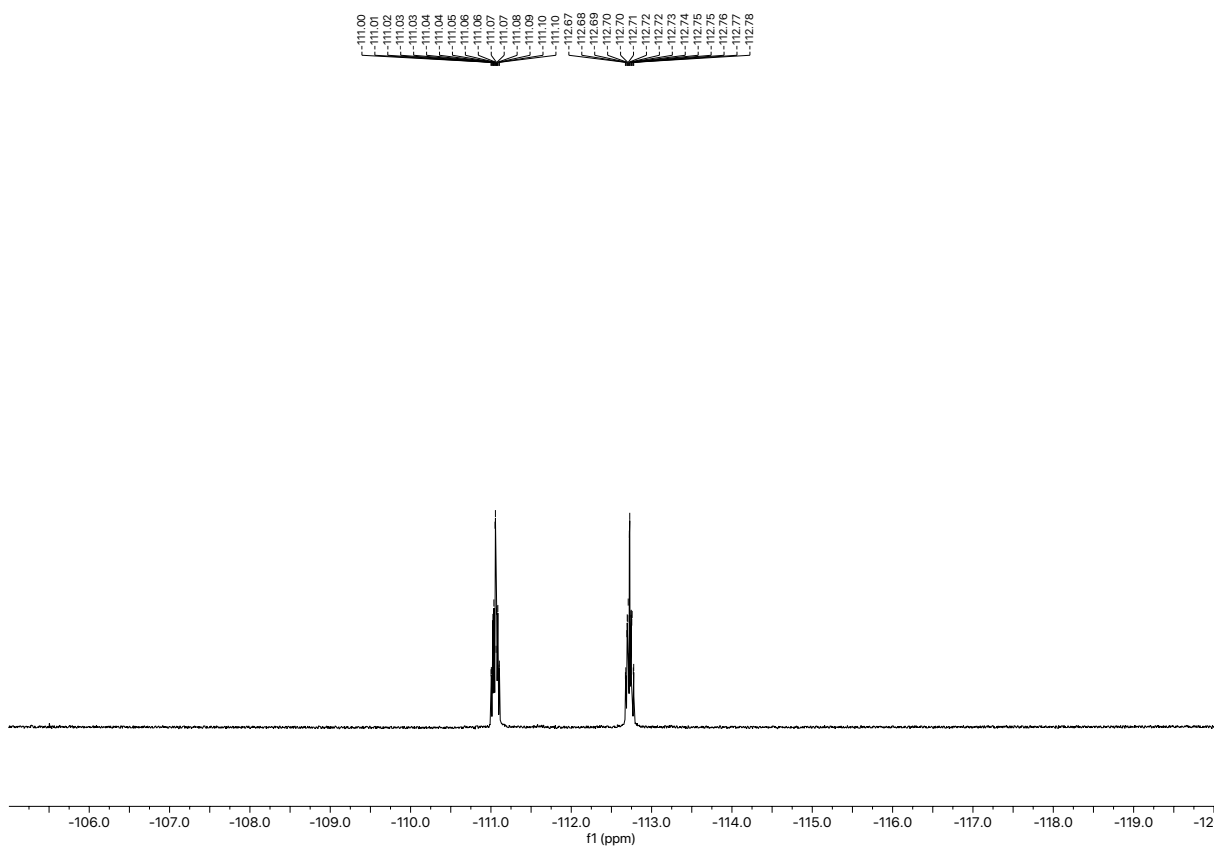
Infrared spectrum (Thin Film, NaCl) of compound **1b**.¹³C NMR (100 MHz, CDCl₃) of compound **1b**.



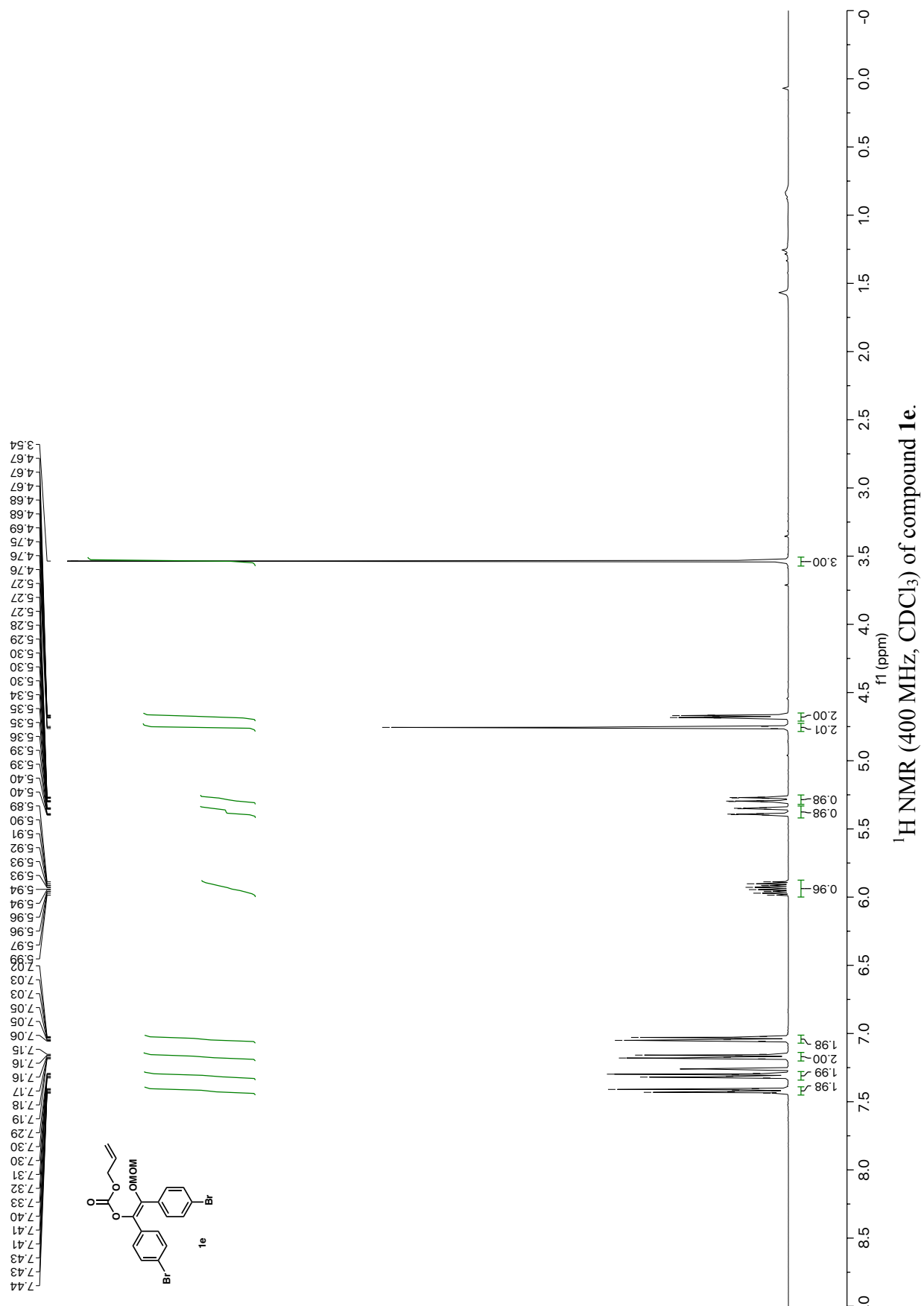
Infrared spectrum (Thin Film, NaCl) of compound **1c**.¹³C NMR (100 MHz, CDCl₃) of compound **1c**.

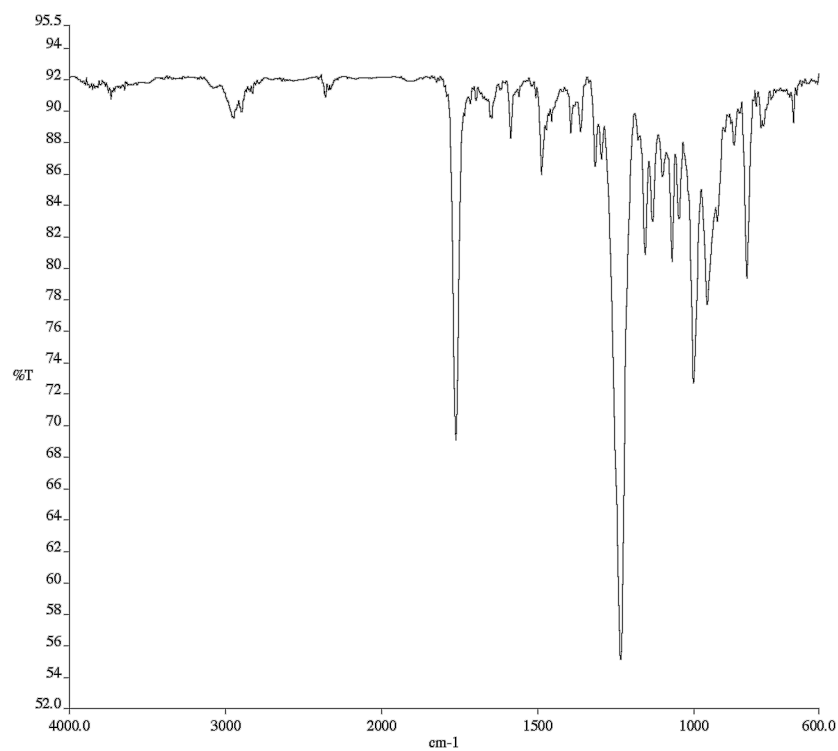
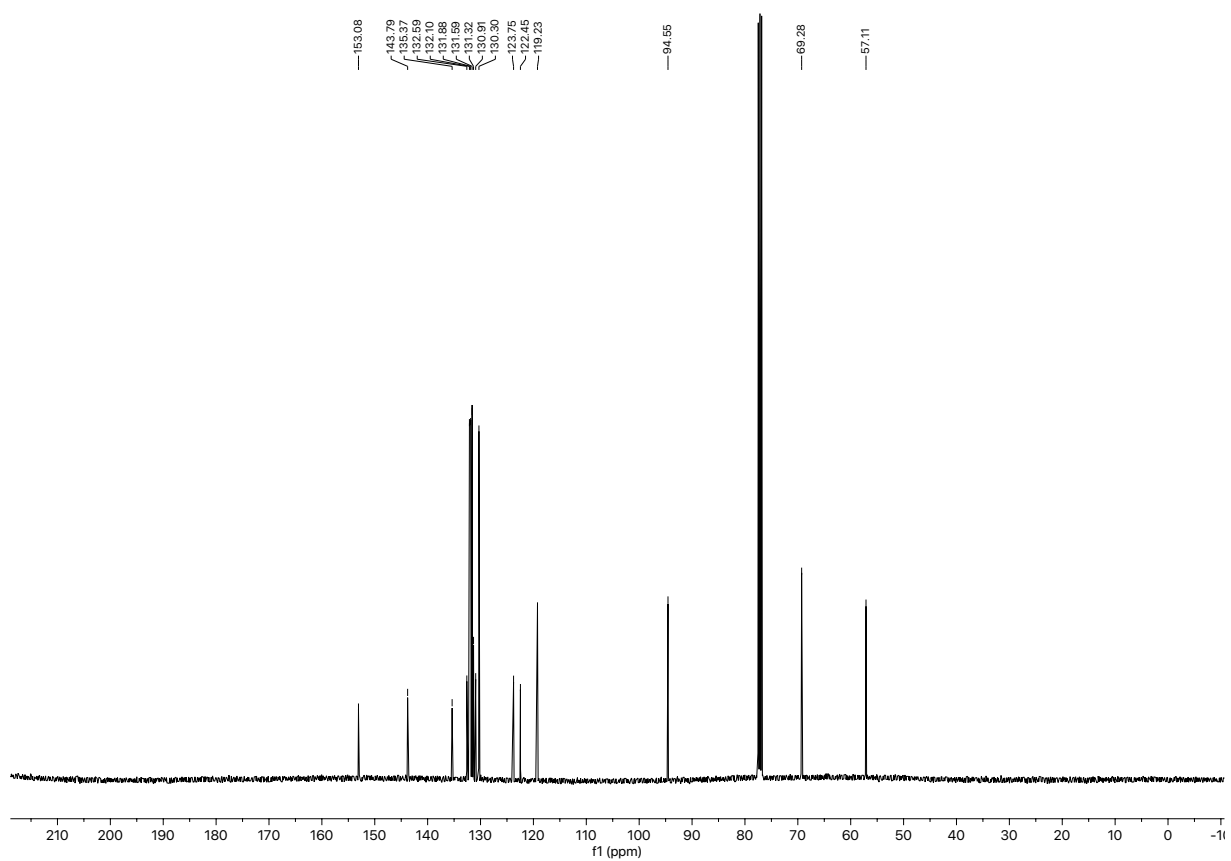


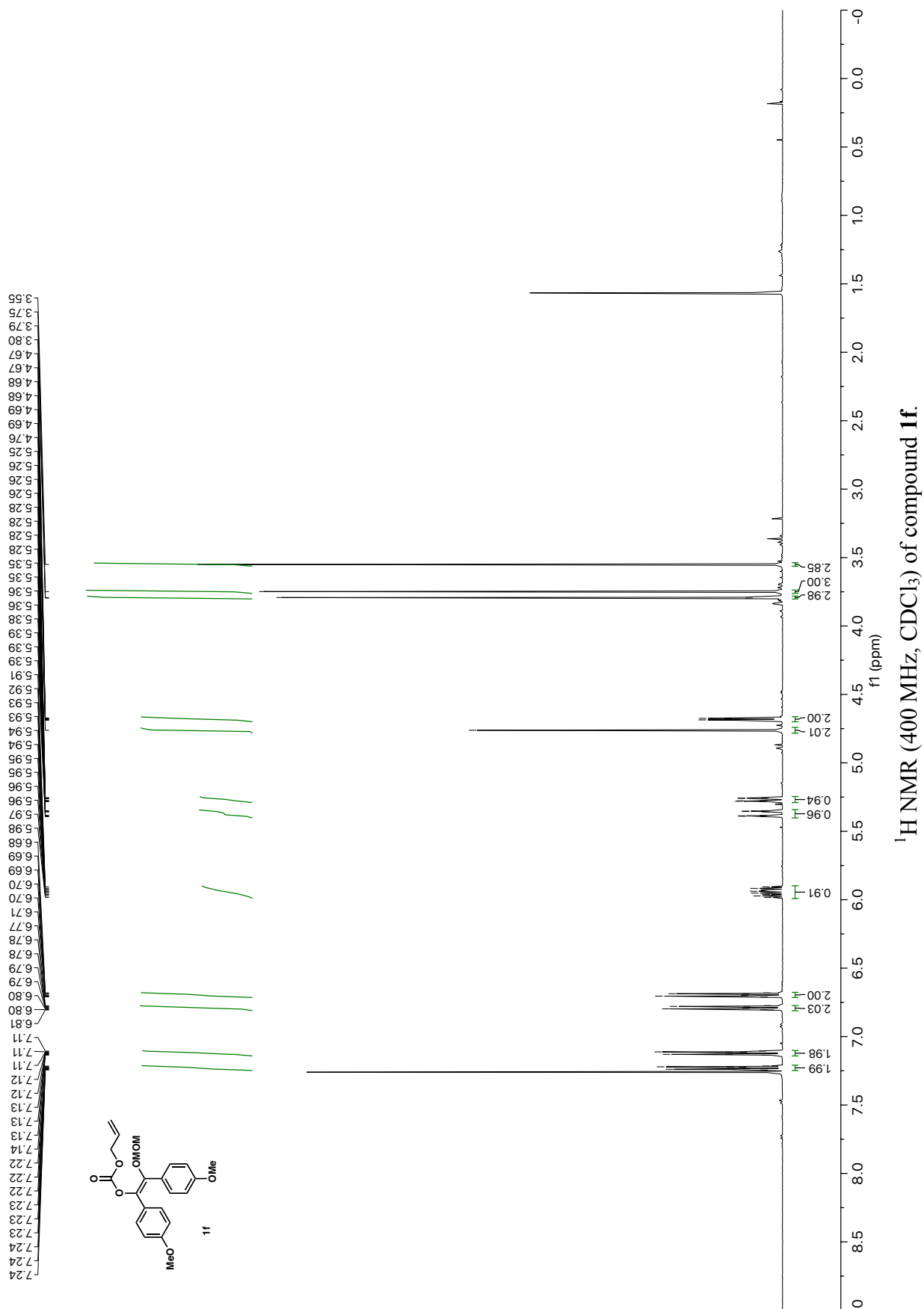
Infrared spectrum (Thin Film, NaCl) of compound **1d**.¹³C NMR (100 MHz, CDCl₃) of compound **1d**.

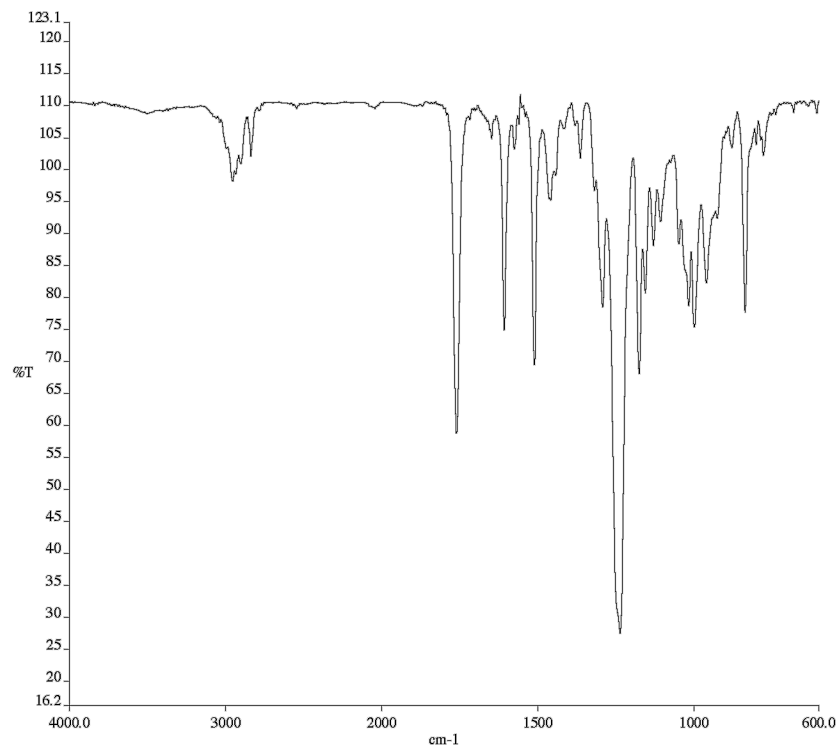
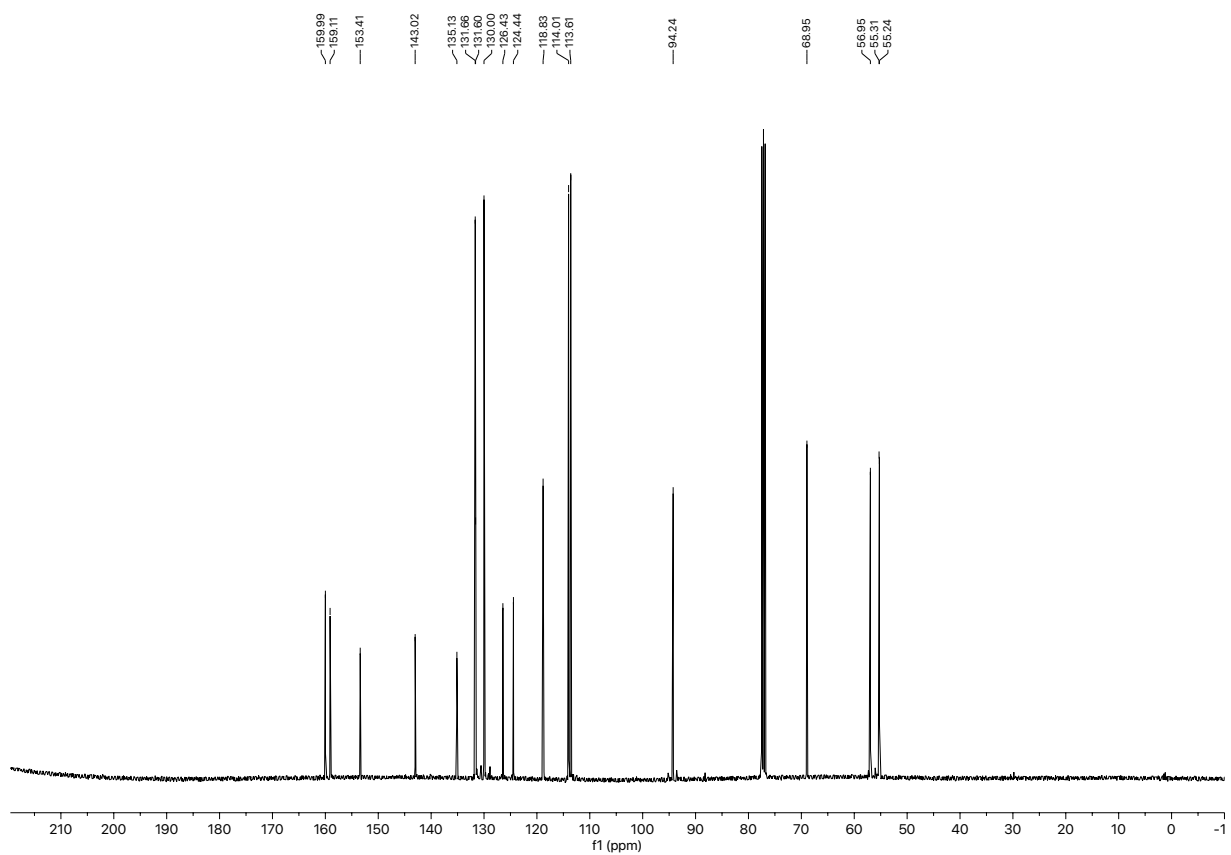


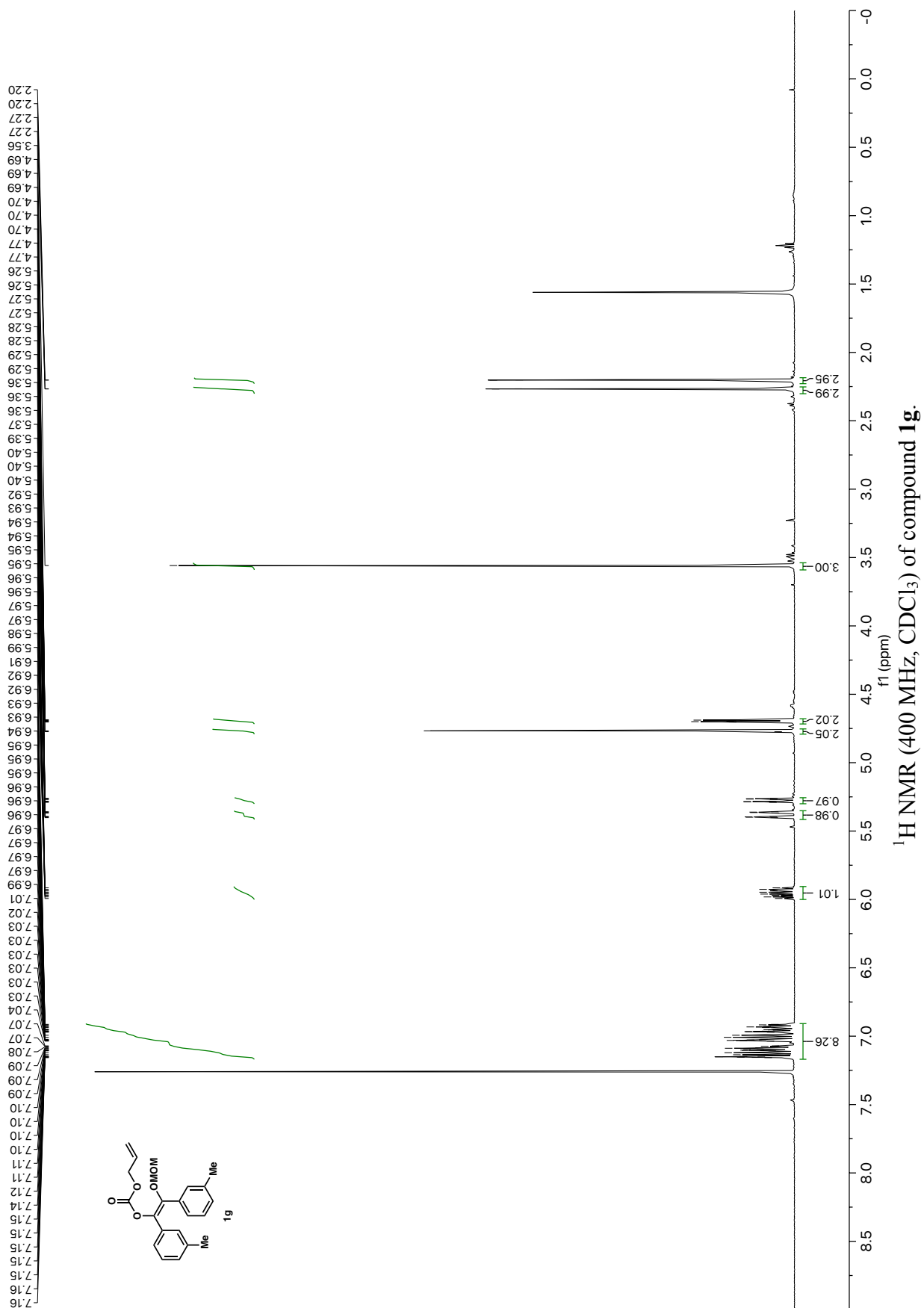
^{19}F NMR (282 MHz, CDCl_3) of compound **1d**.

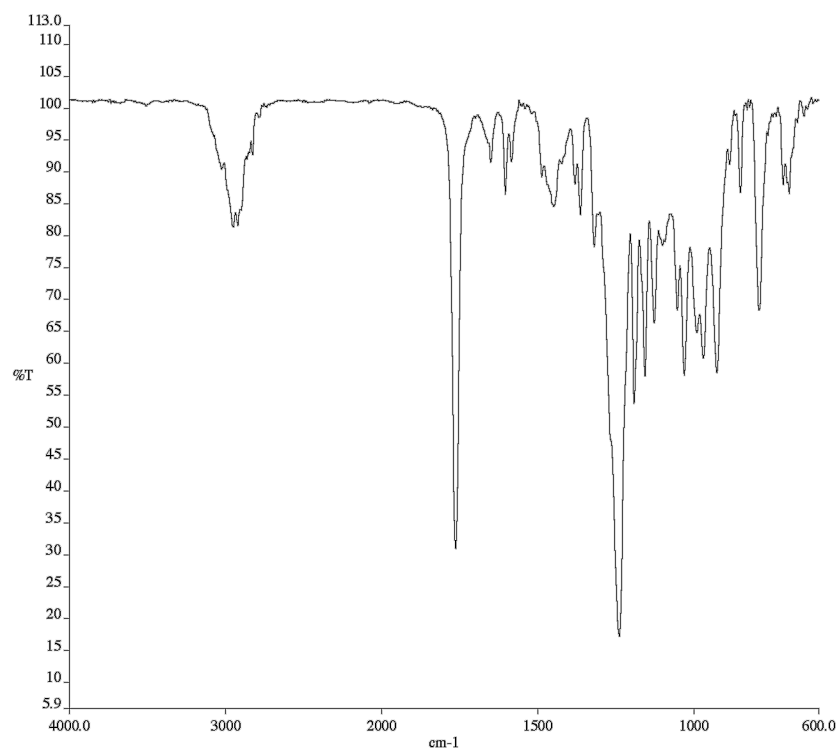
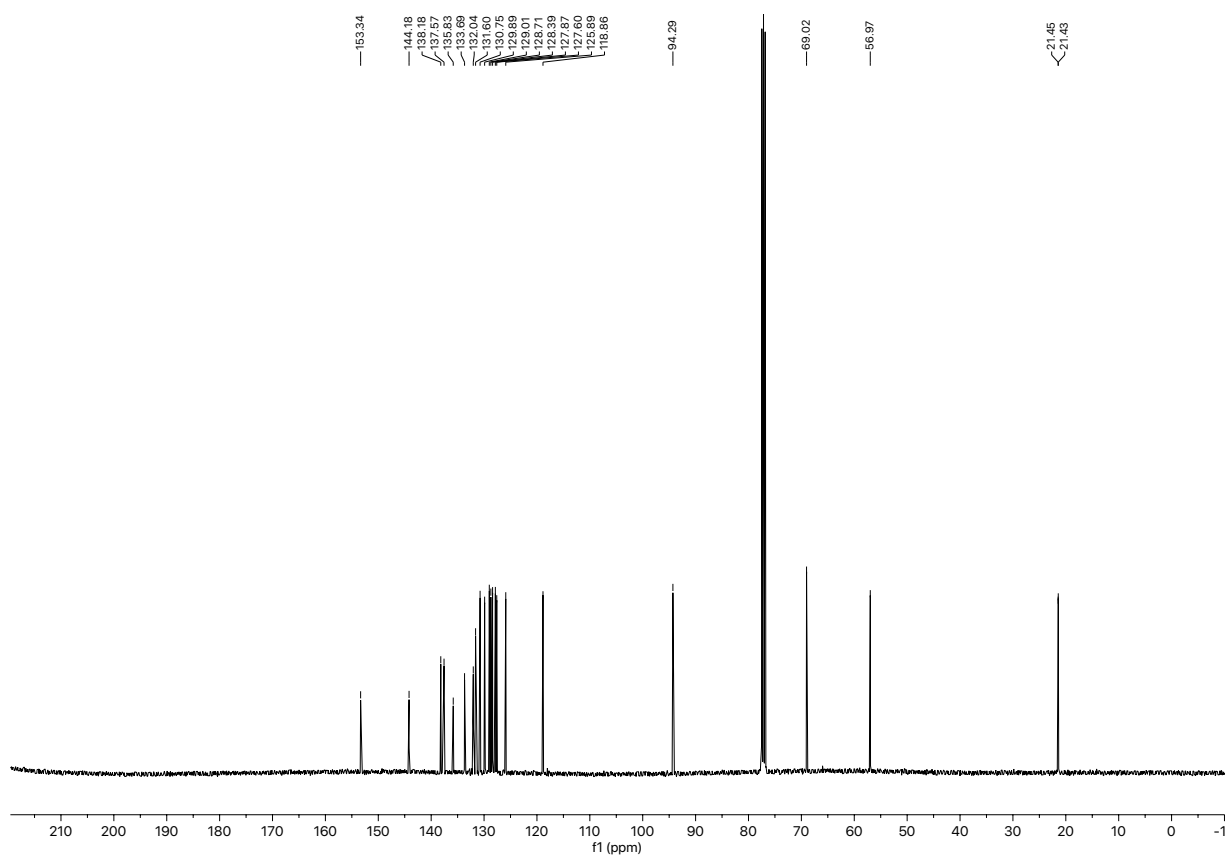


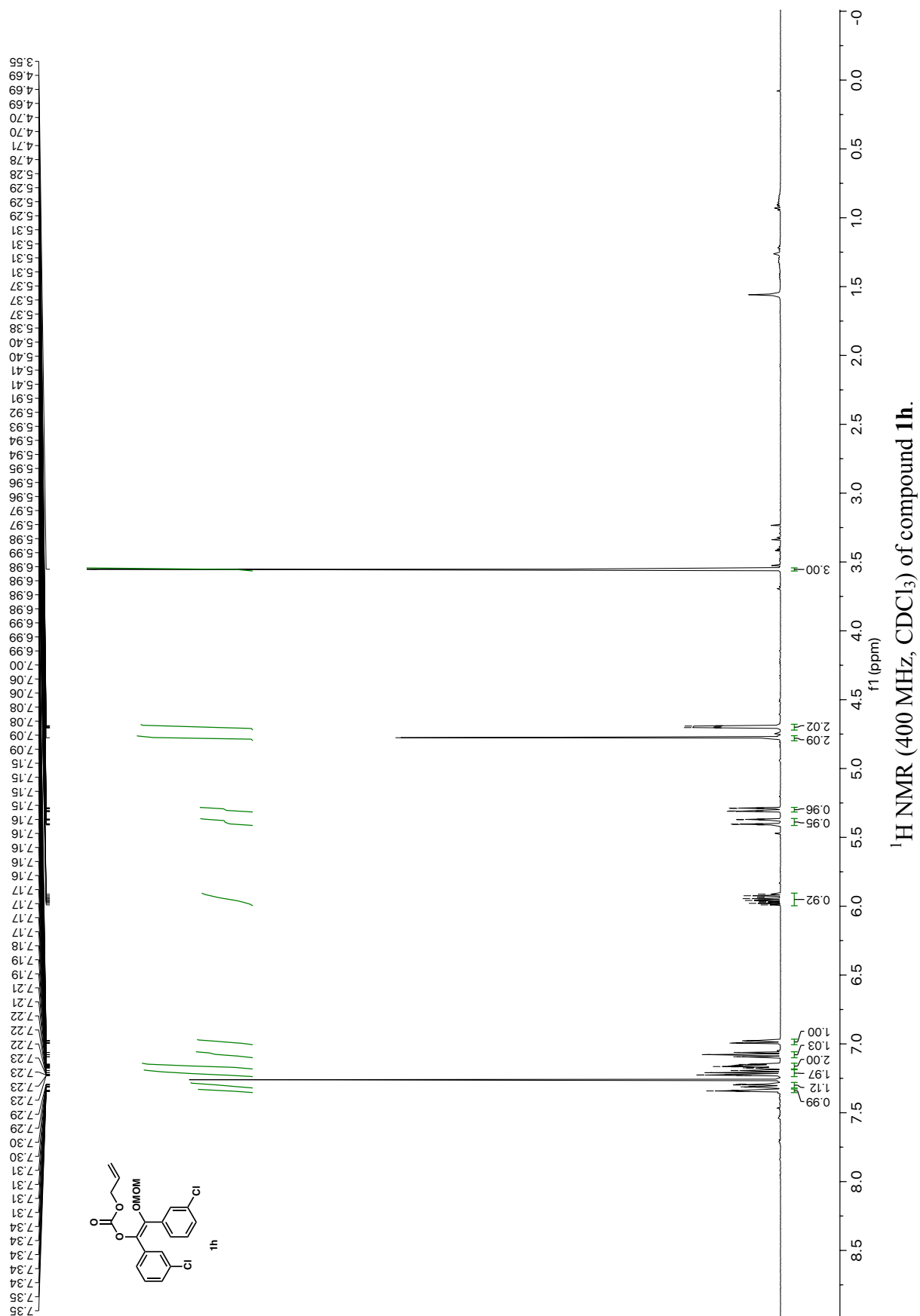
Infrared spectrum (Thin Film, NaCl) of compound **1e**.¹³C NMR (100 MHz, CDCl₃) of compound **1e**.

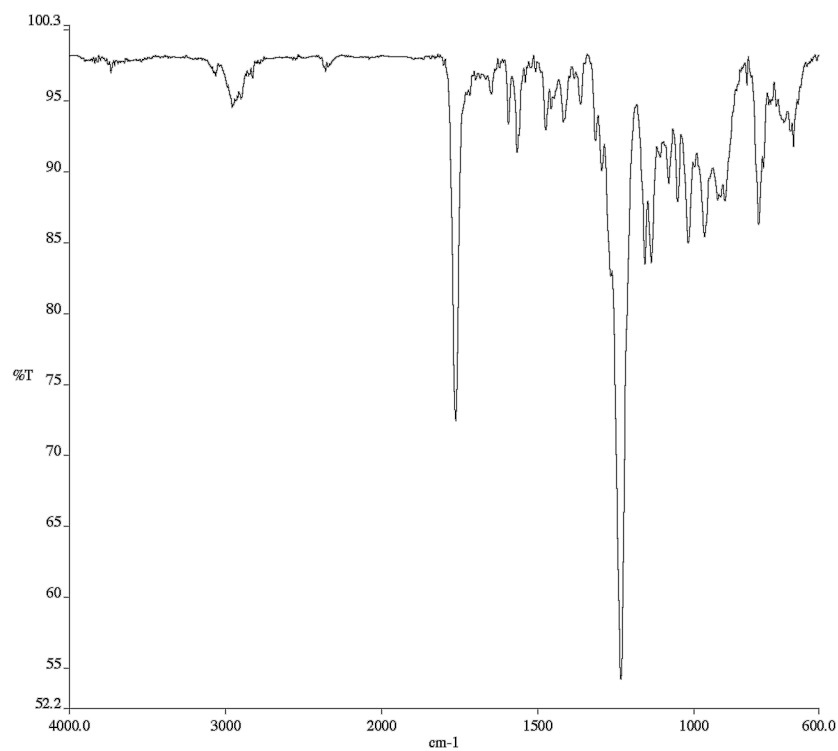
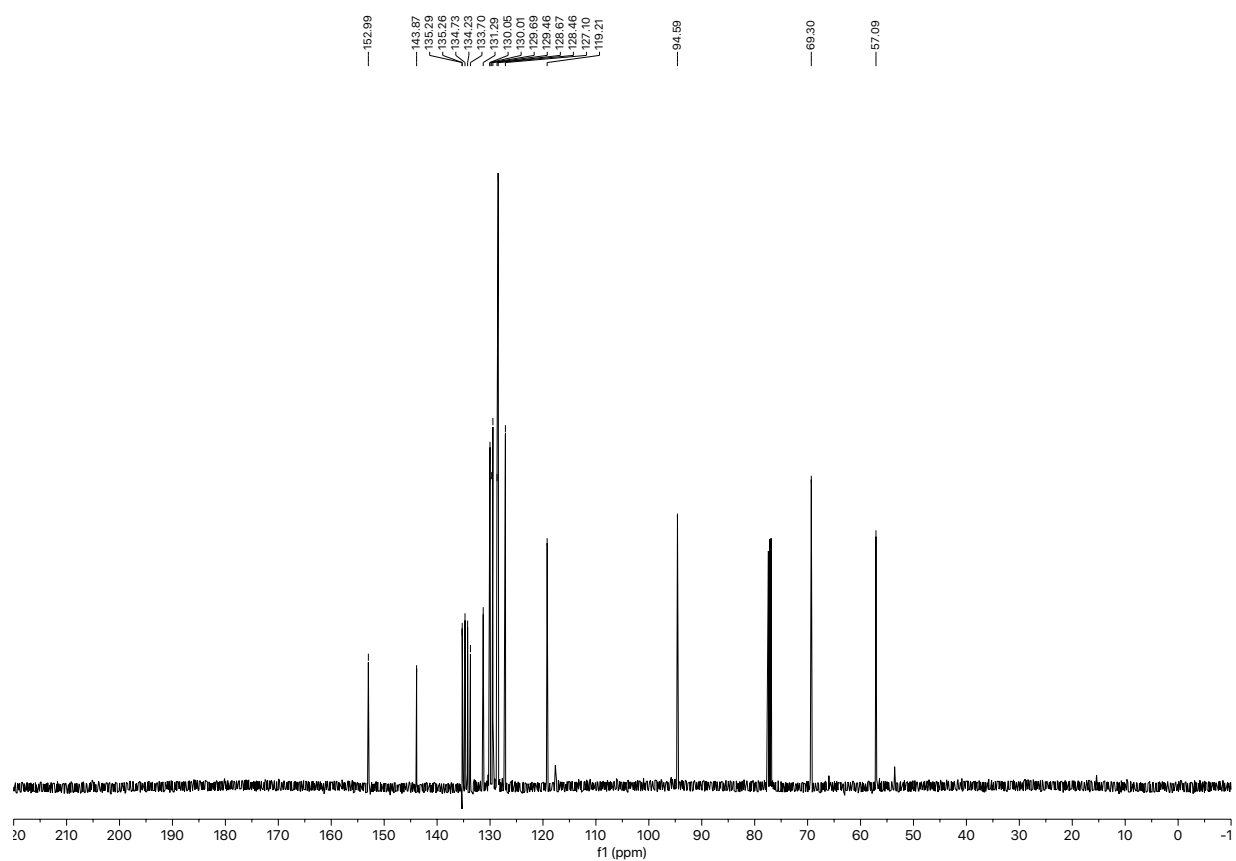


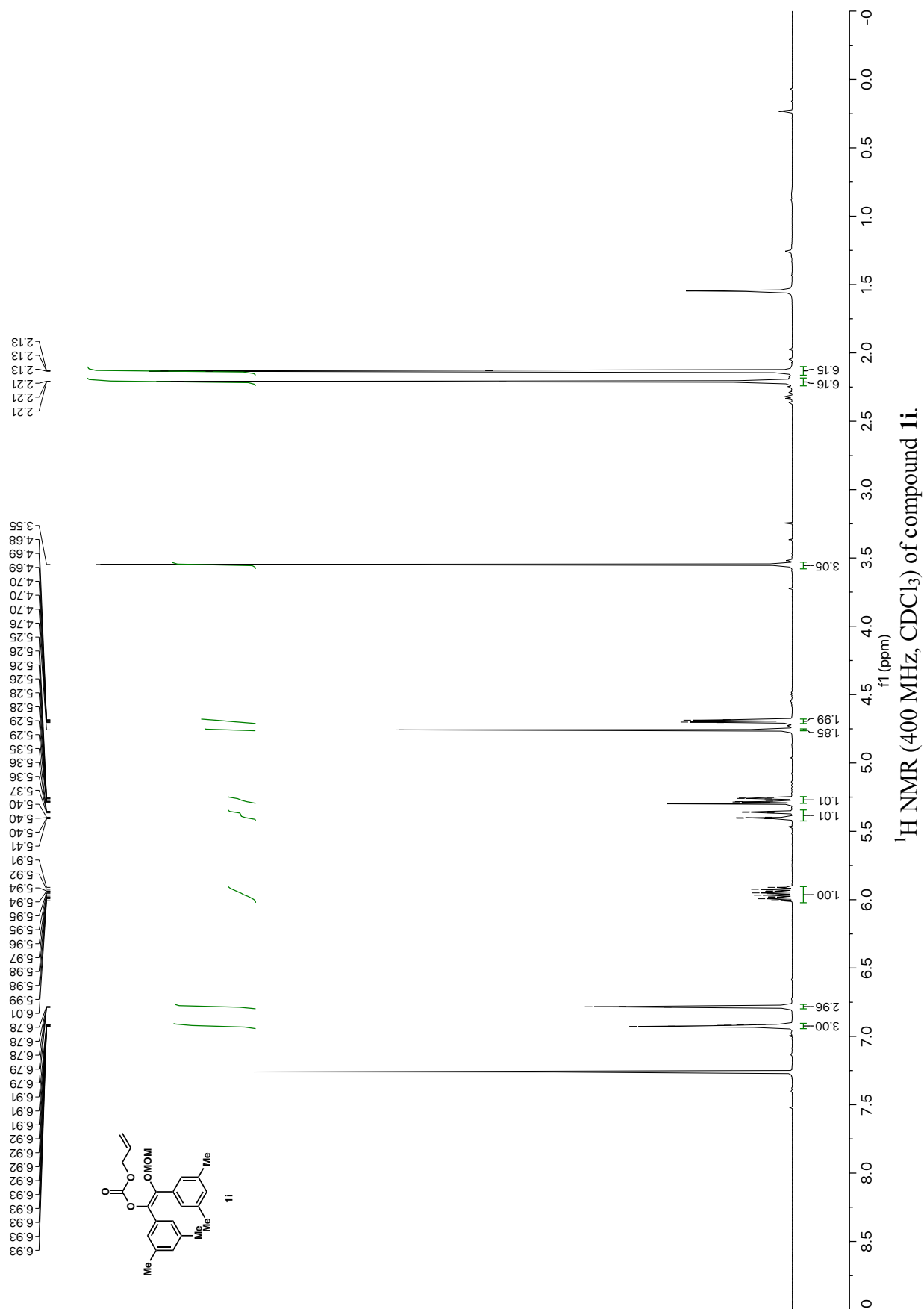
Infrared spectrum (Thin Film, NaCl) of compound **1f**.¹³C NMR (100 MHz, CDCl₃) of compound **1f**.

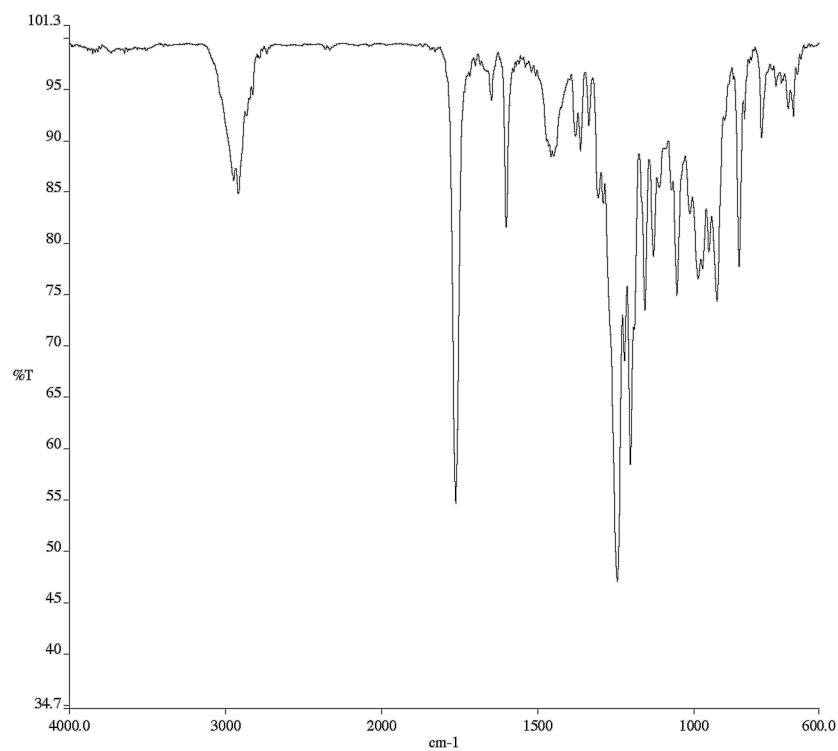
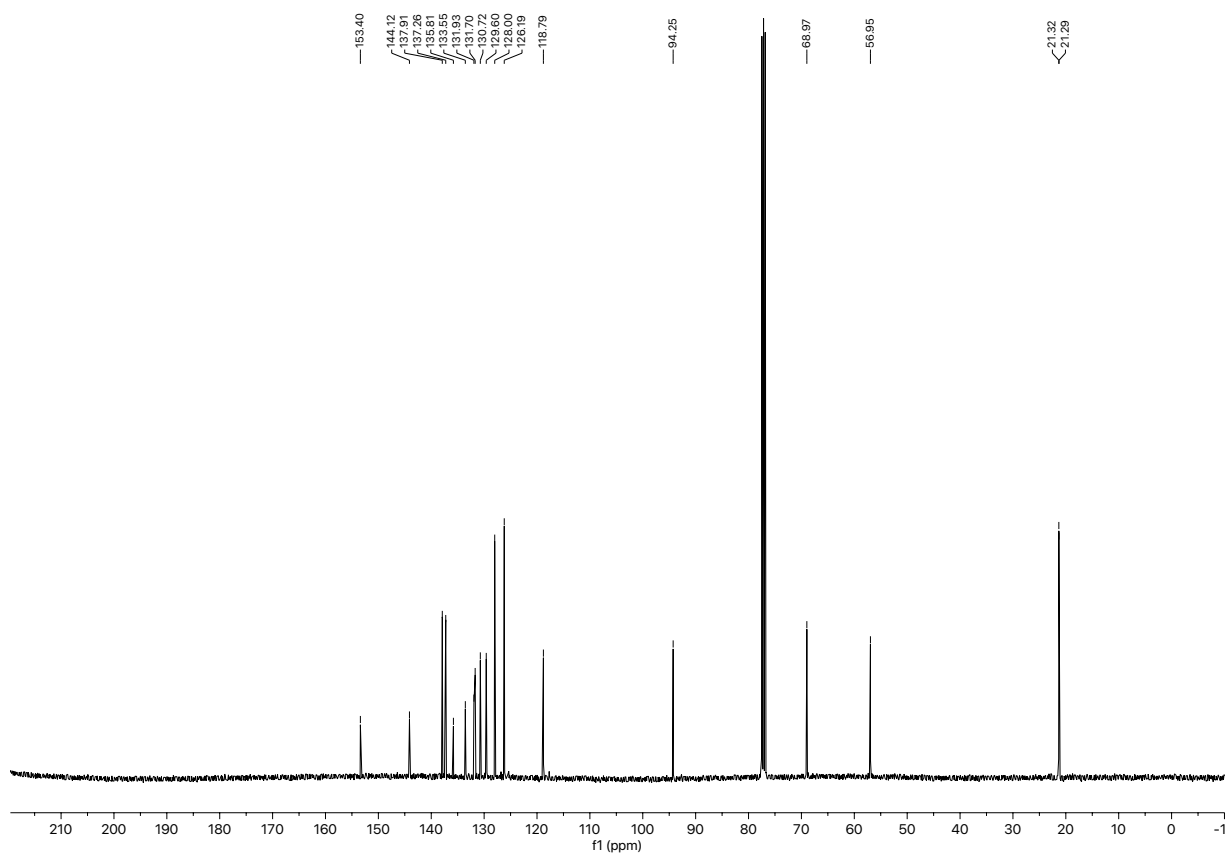


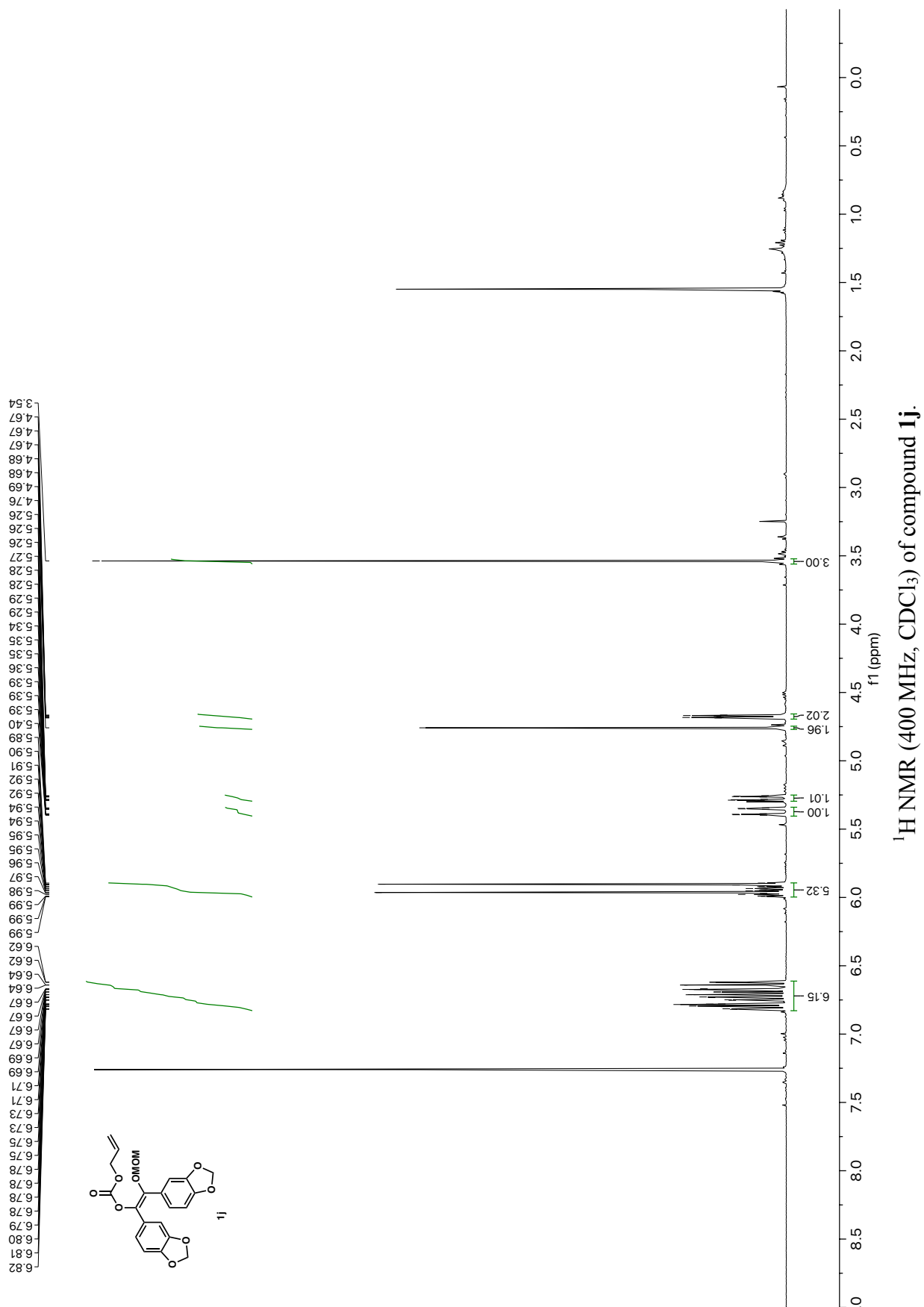
Infrared spectrum (Thin Film, NaCl) of compound **1g**.¹³C NMR (100 MHz, CDCl₃) of compound **1g**.

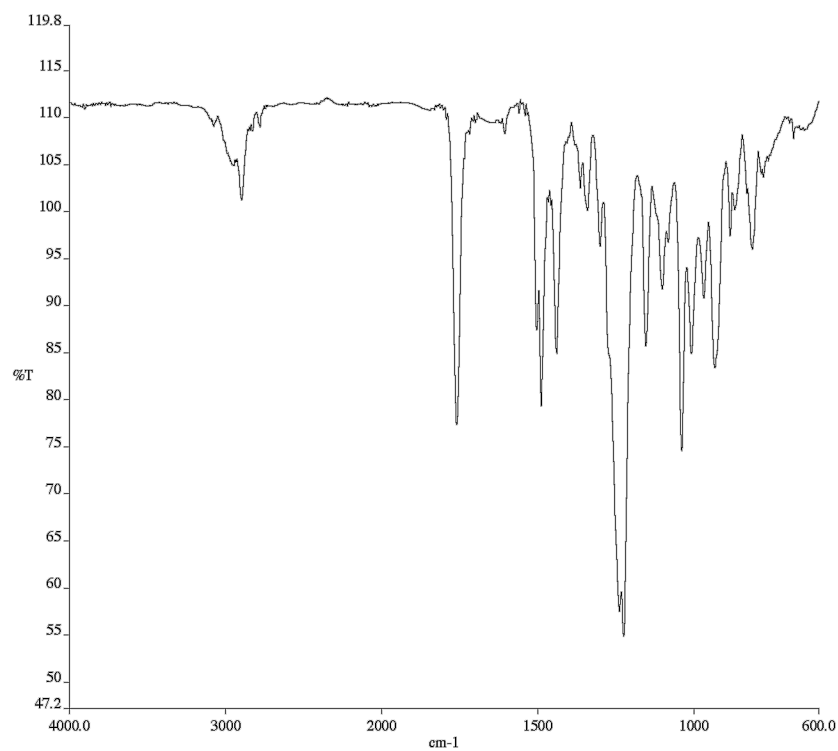
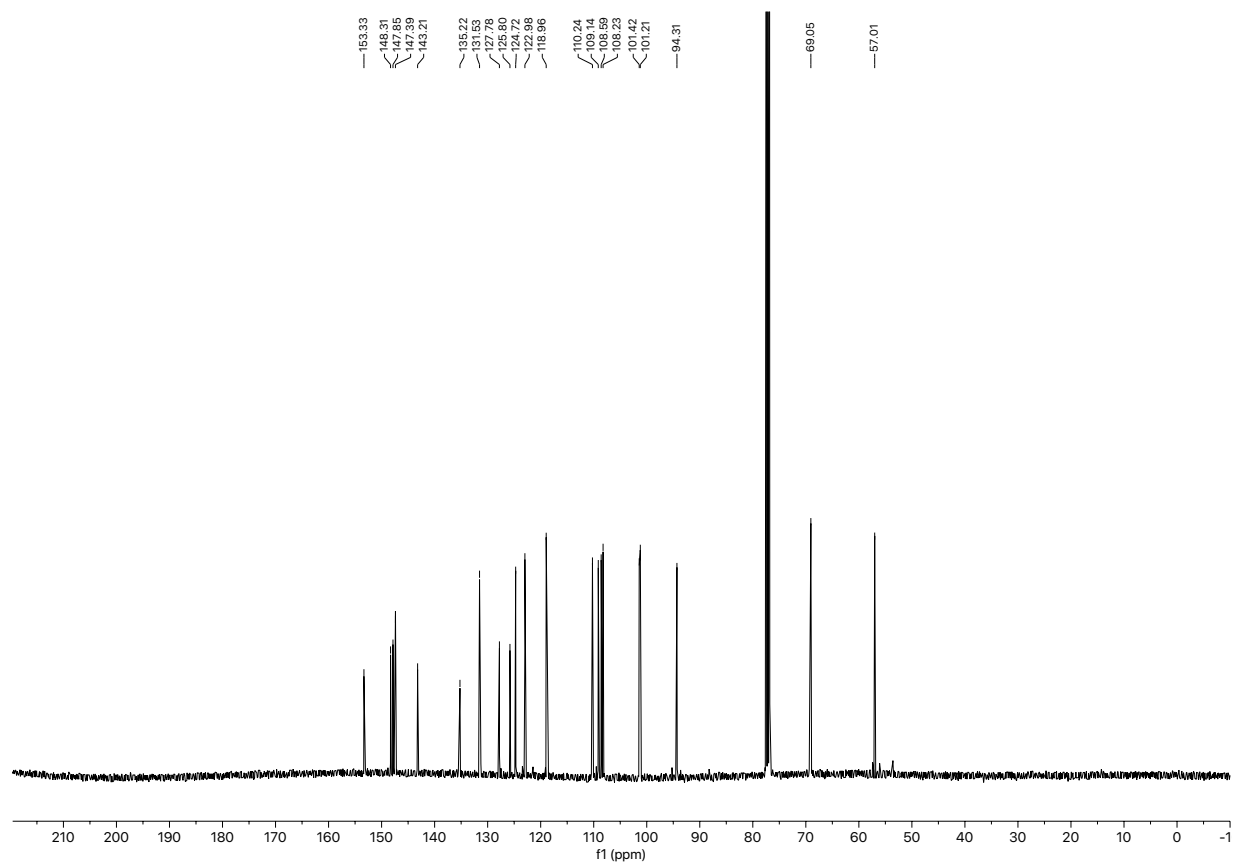


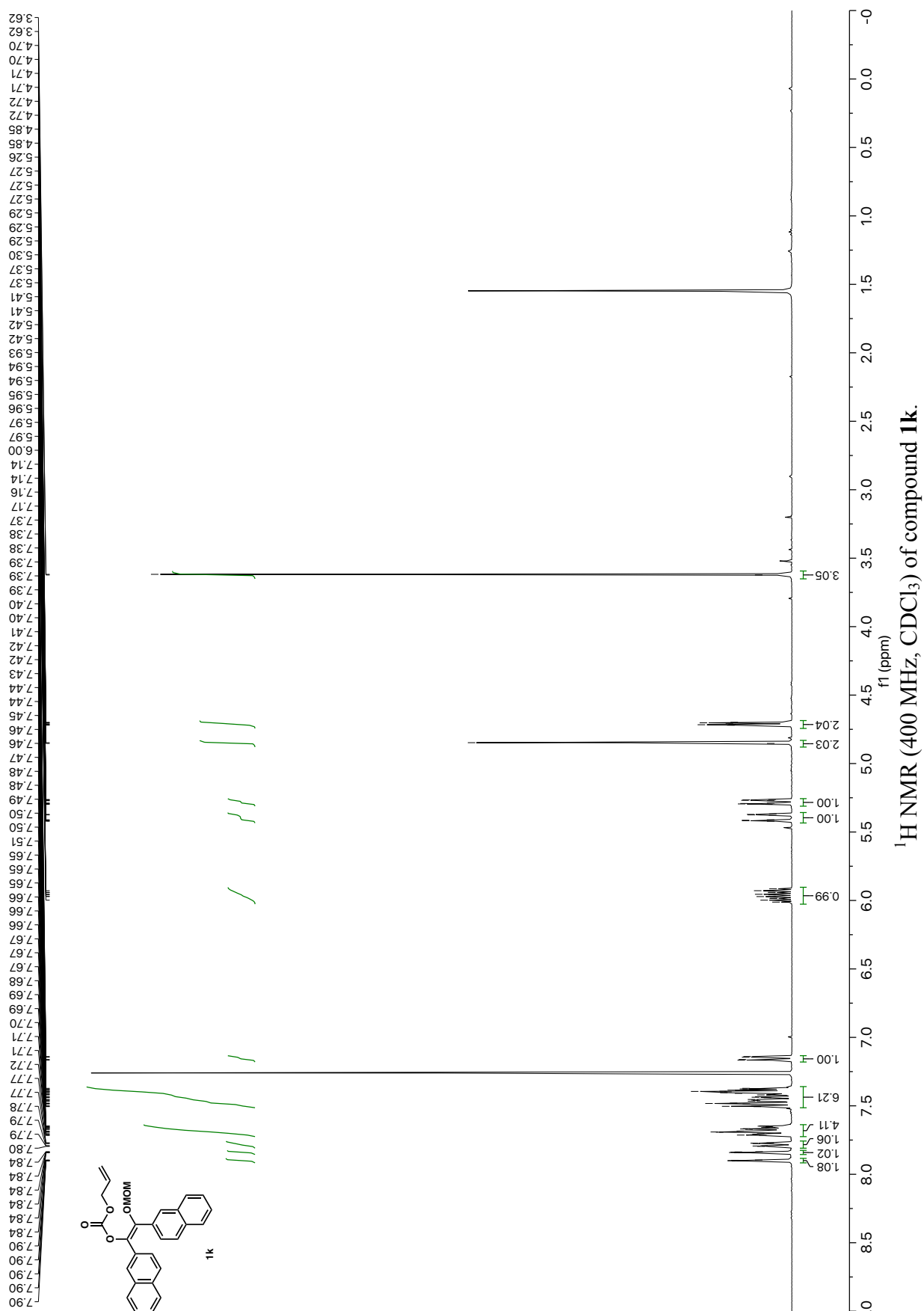
Infrared spectrum (Thin Film, NaCl) of compound **1h**.¹³C NMR (100 MHz, CDCl₃) of compound **1h**.

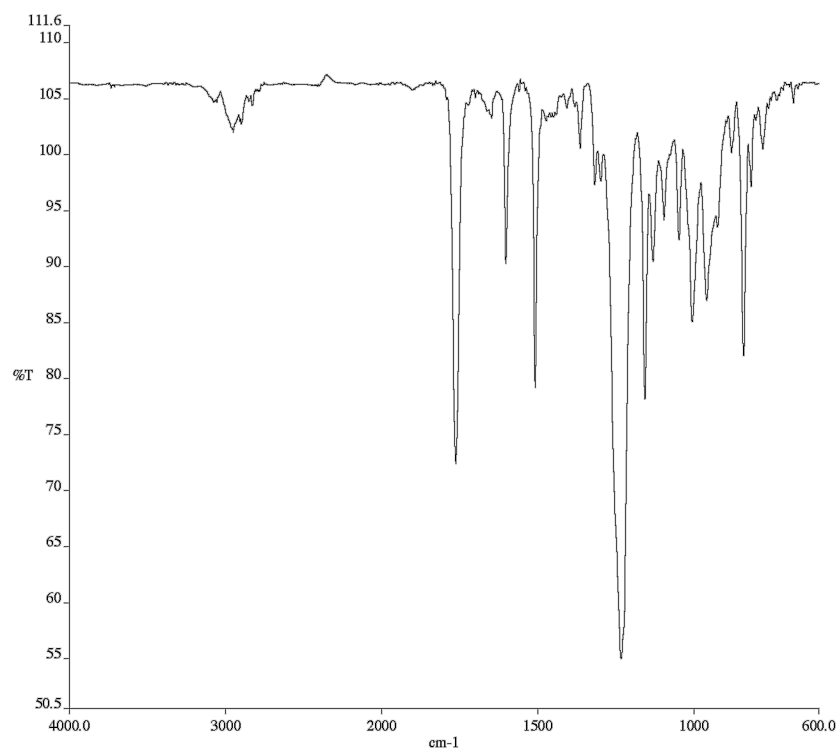
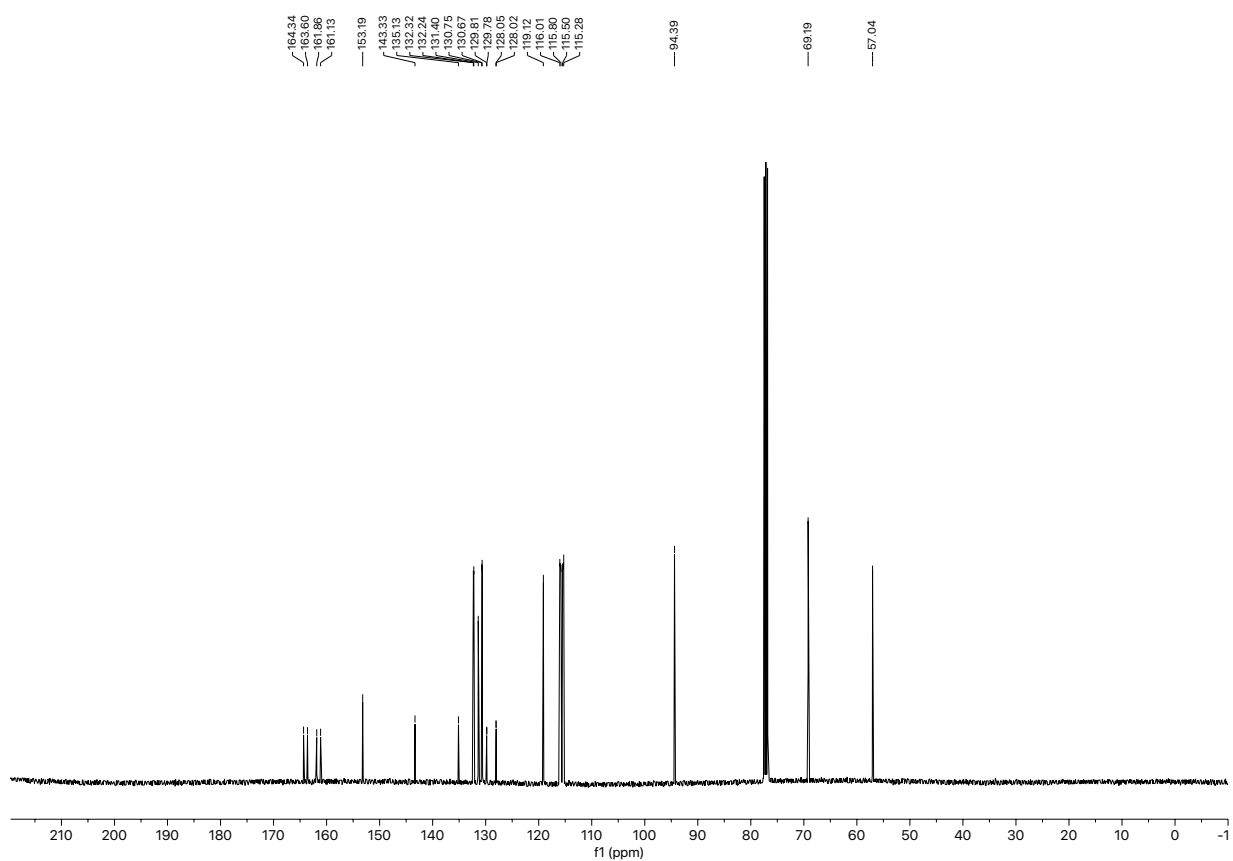


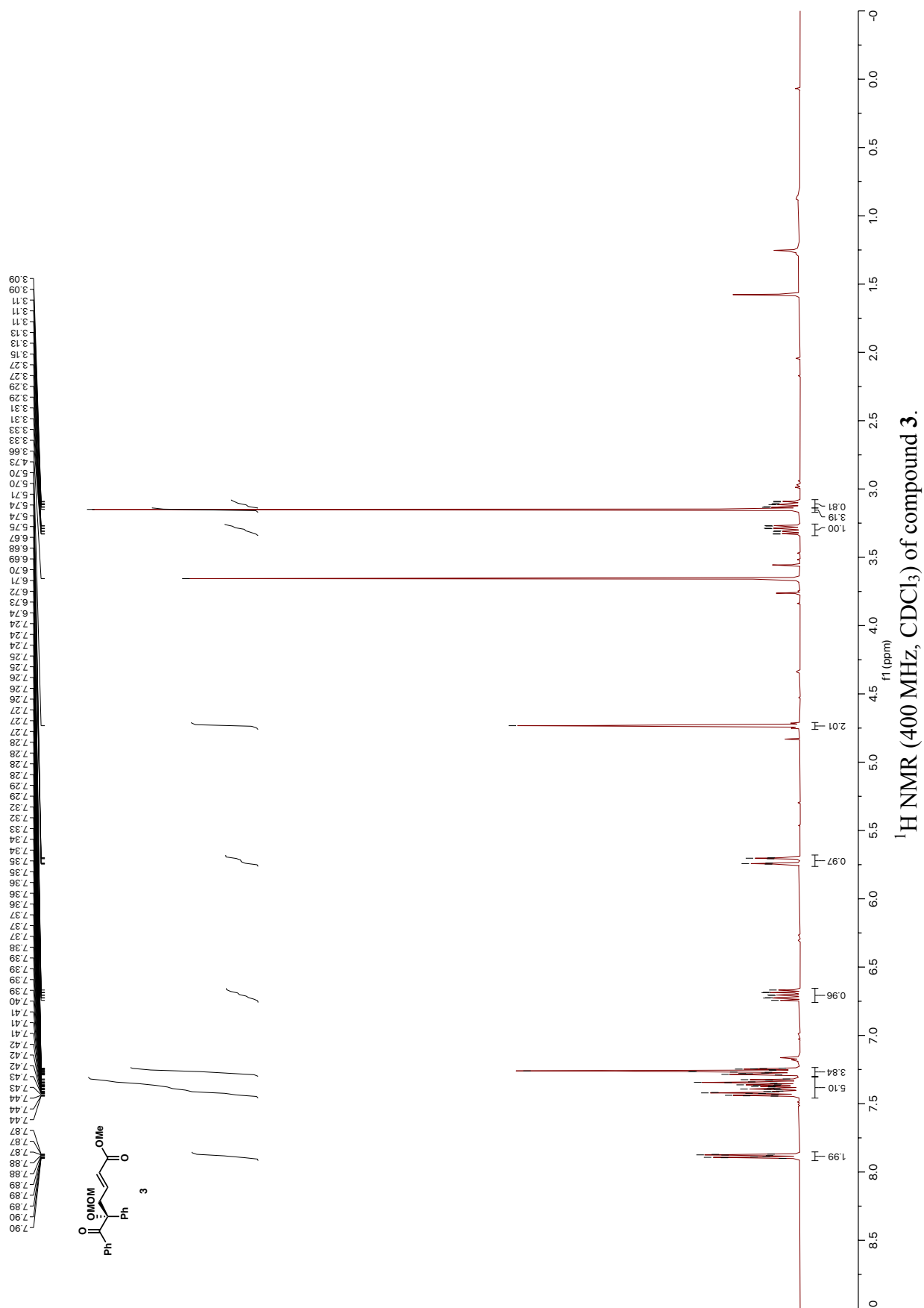
Infrared spectrum (Thin Film, NaCl) of compound **1i**.¹³C NMR (100 MHz, CDCl₃) of compound **1i**.

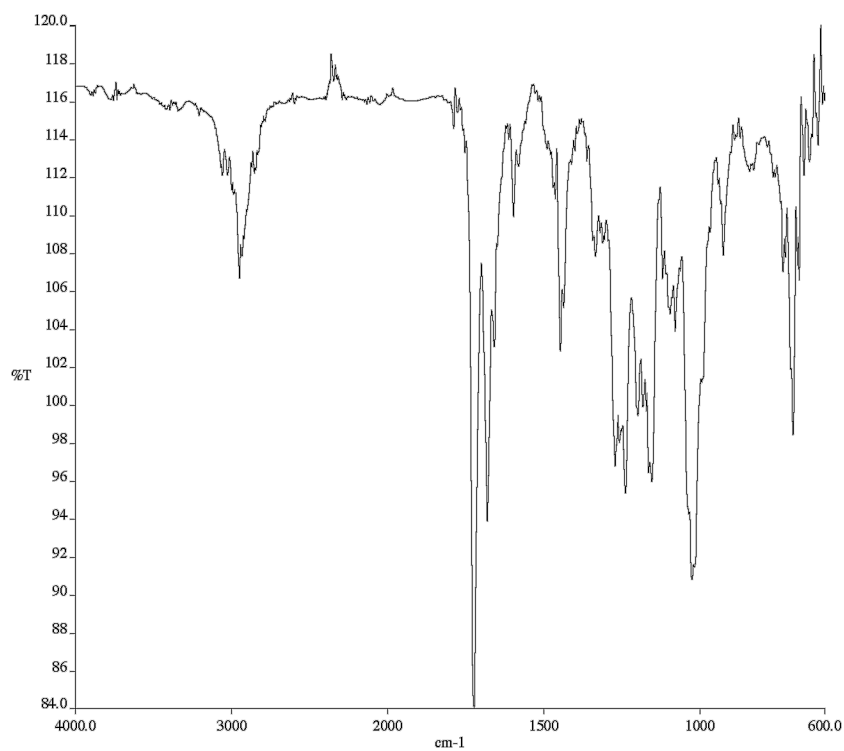
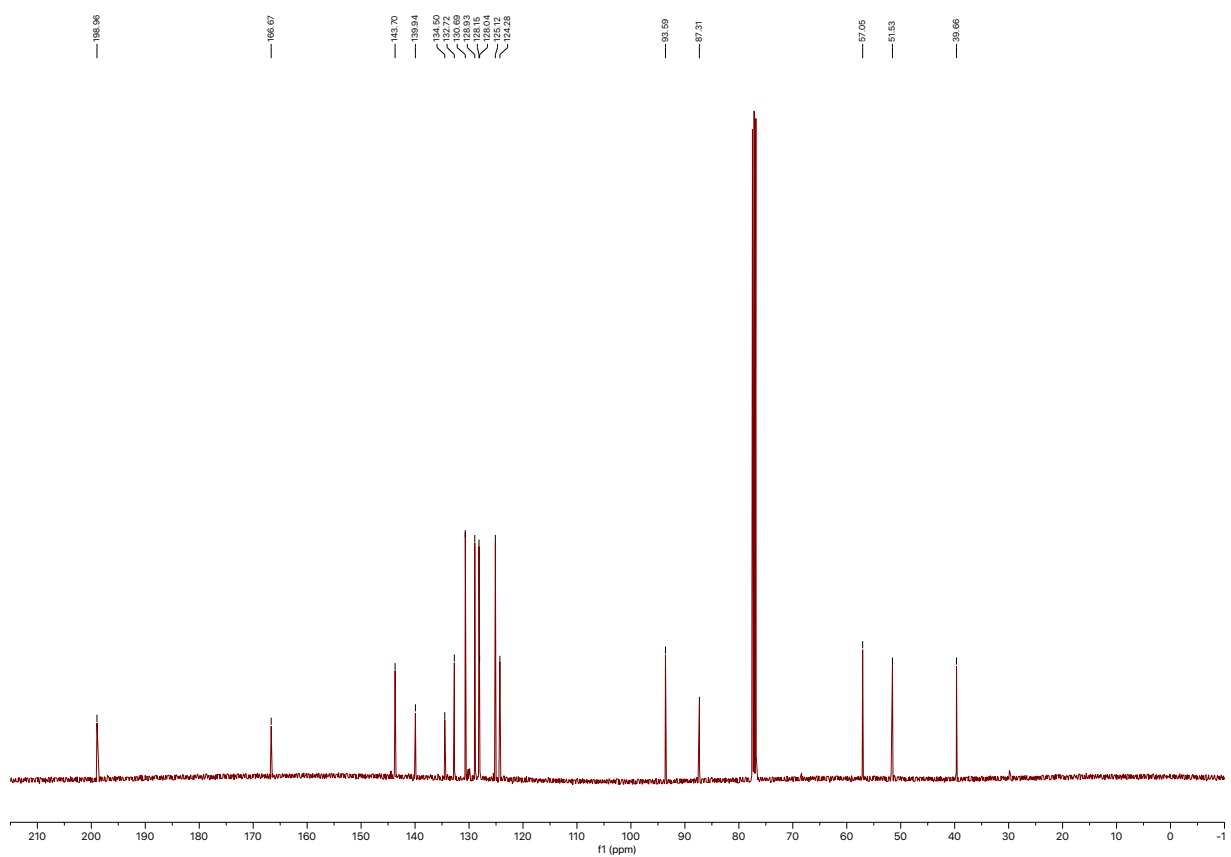


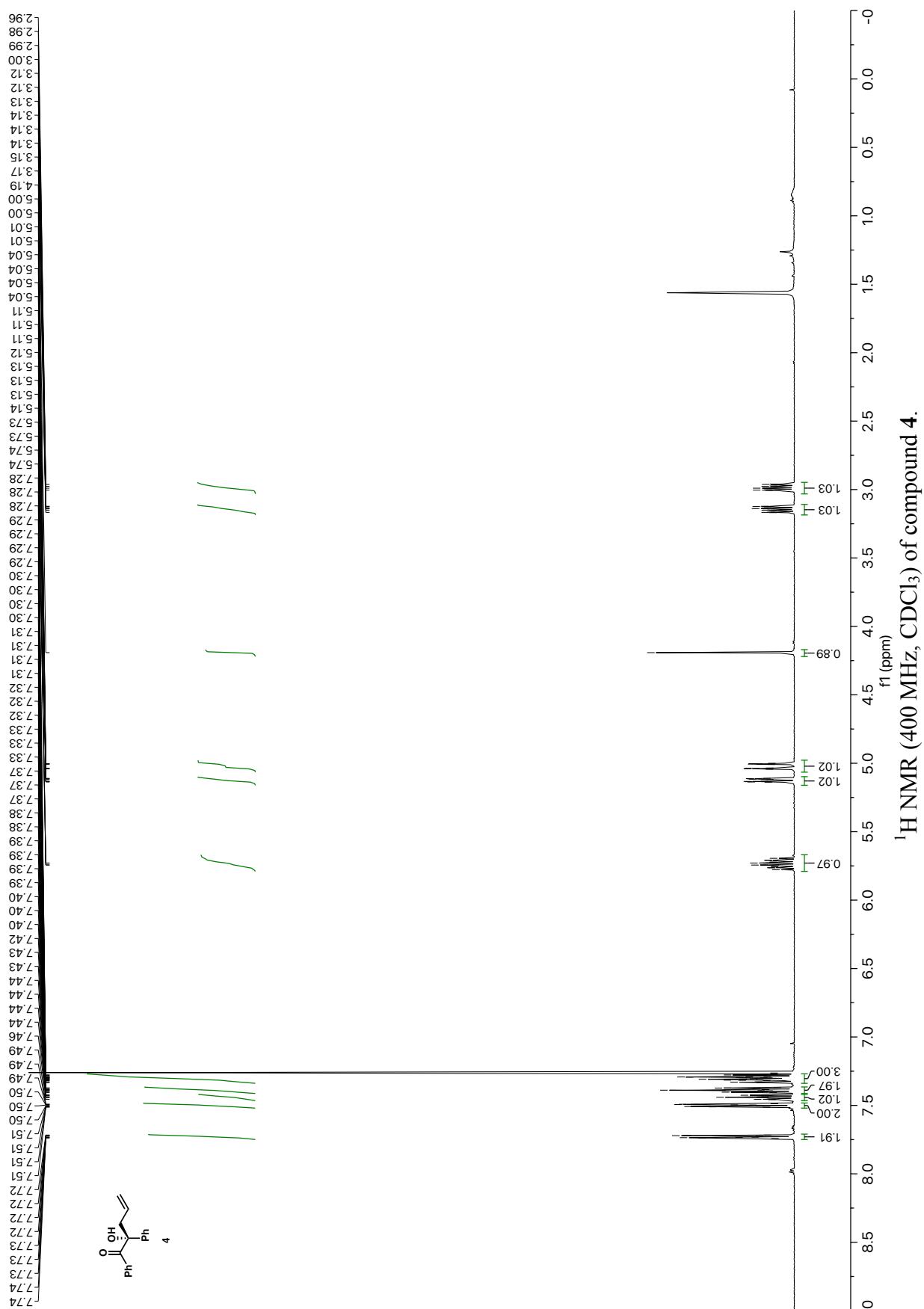
Infrared spectrum (Thin Film, NaCl) of compound **1j**.¹³C NMR (100 MHz, CDCl₃) of compound **1j**.

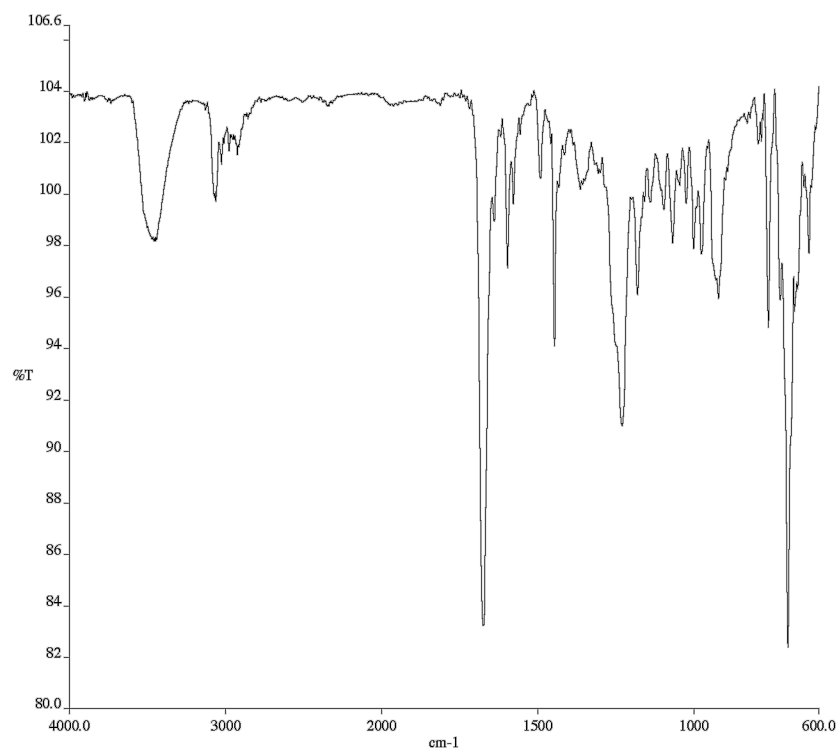


Infrared spectrum (Thin Film, NaCl) of compound **1k**.¹³C NMR (100 MHz, CDCl₃) of compound **1k**.

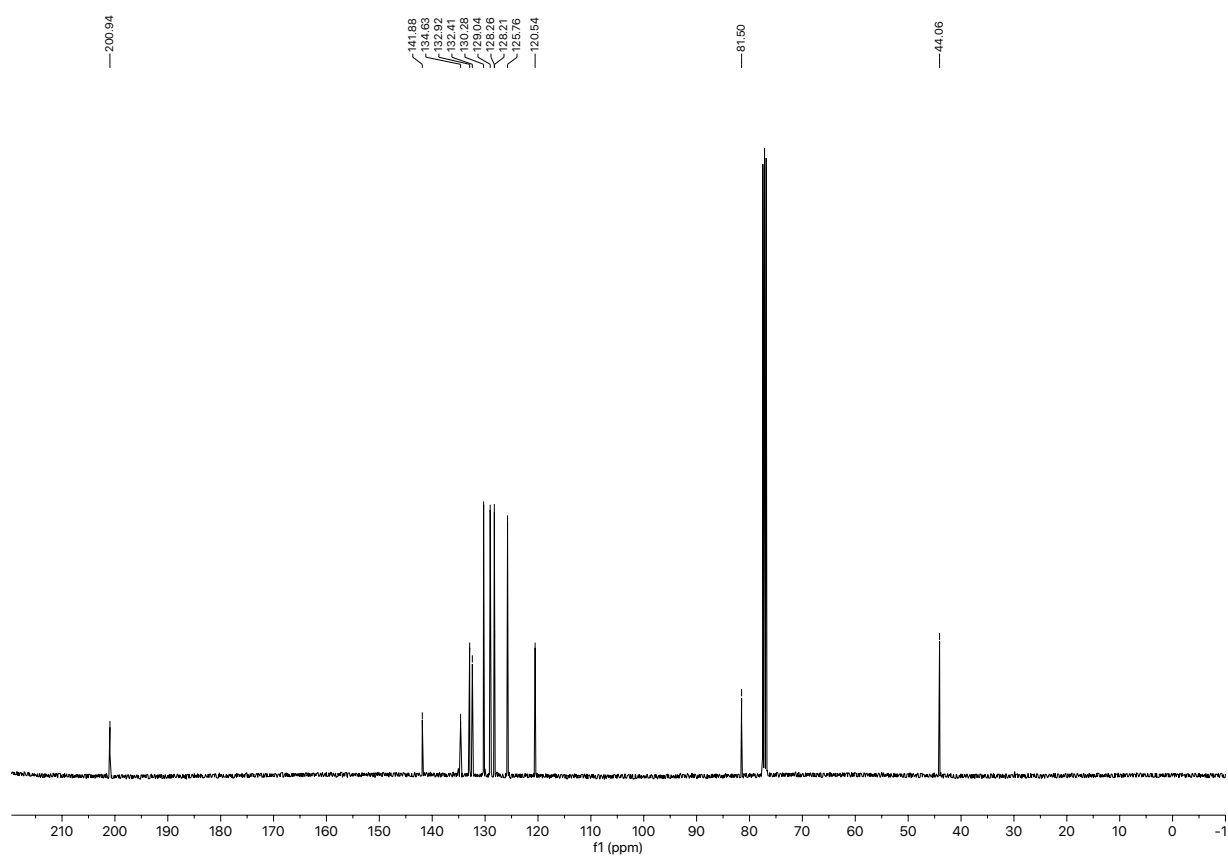


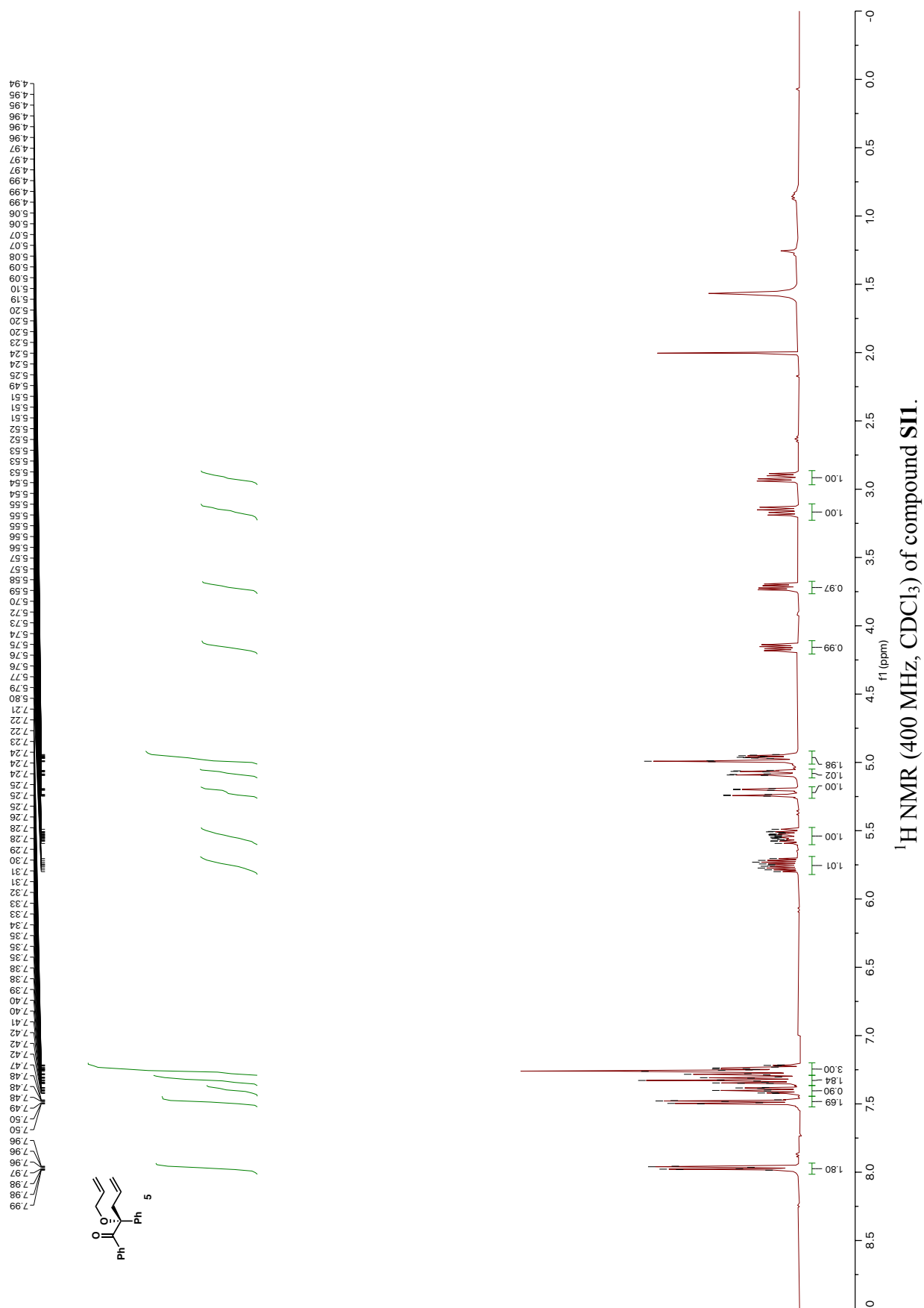
Infrared spectrum (Thin Film, NaCl) of compound **3**.¹³C NMR (100 MHz, CDCl₃) of compound **3**.

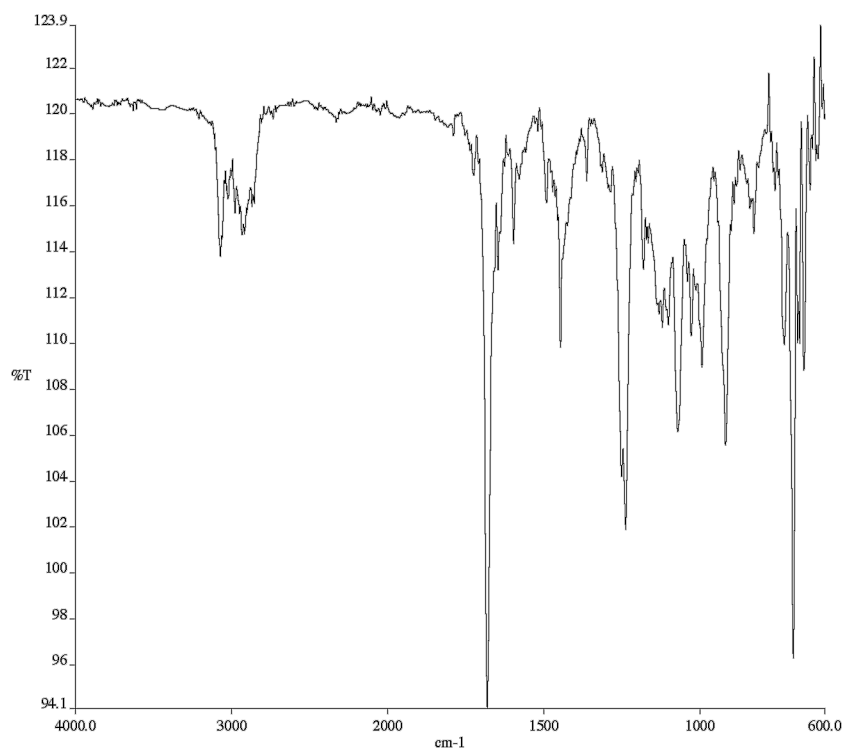
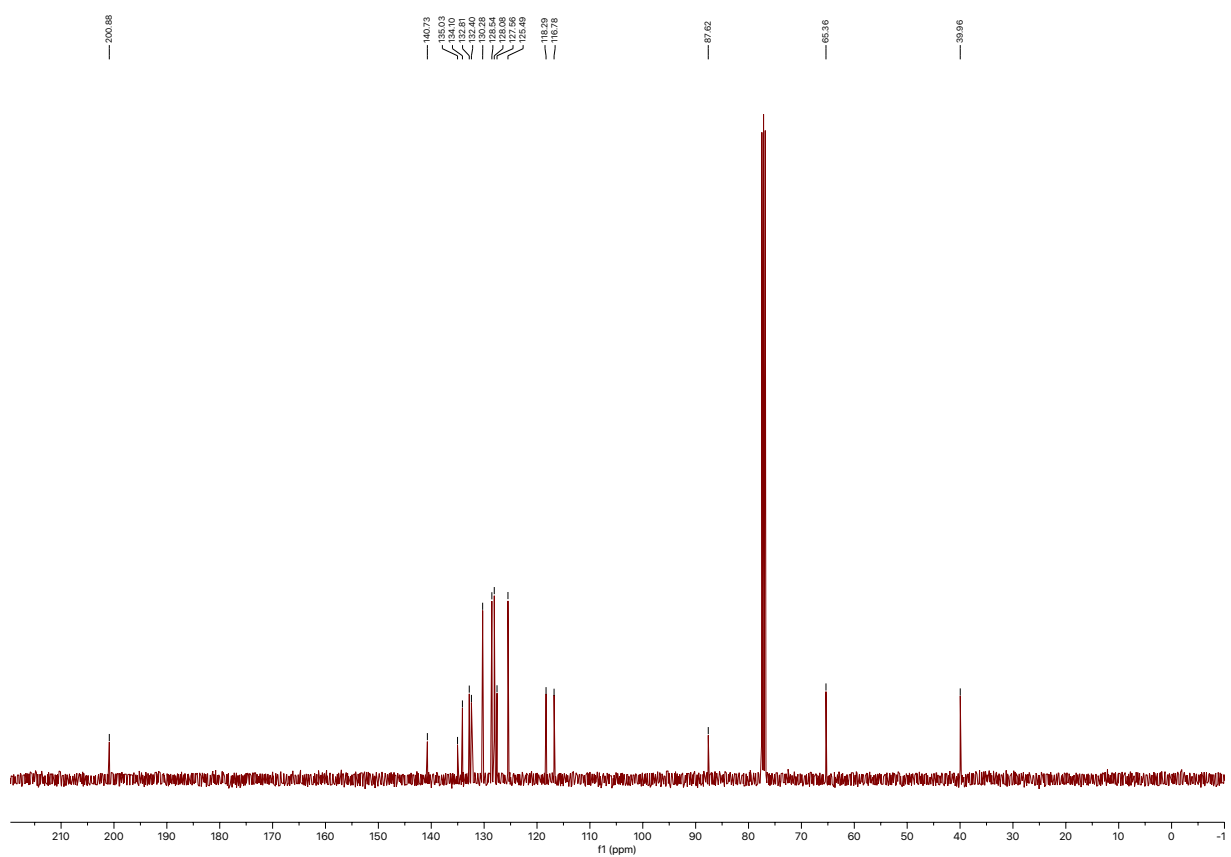


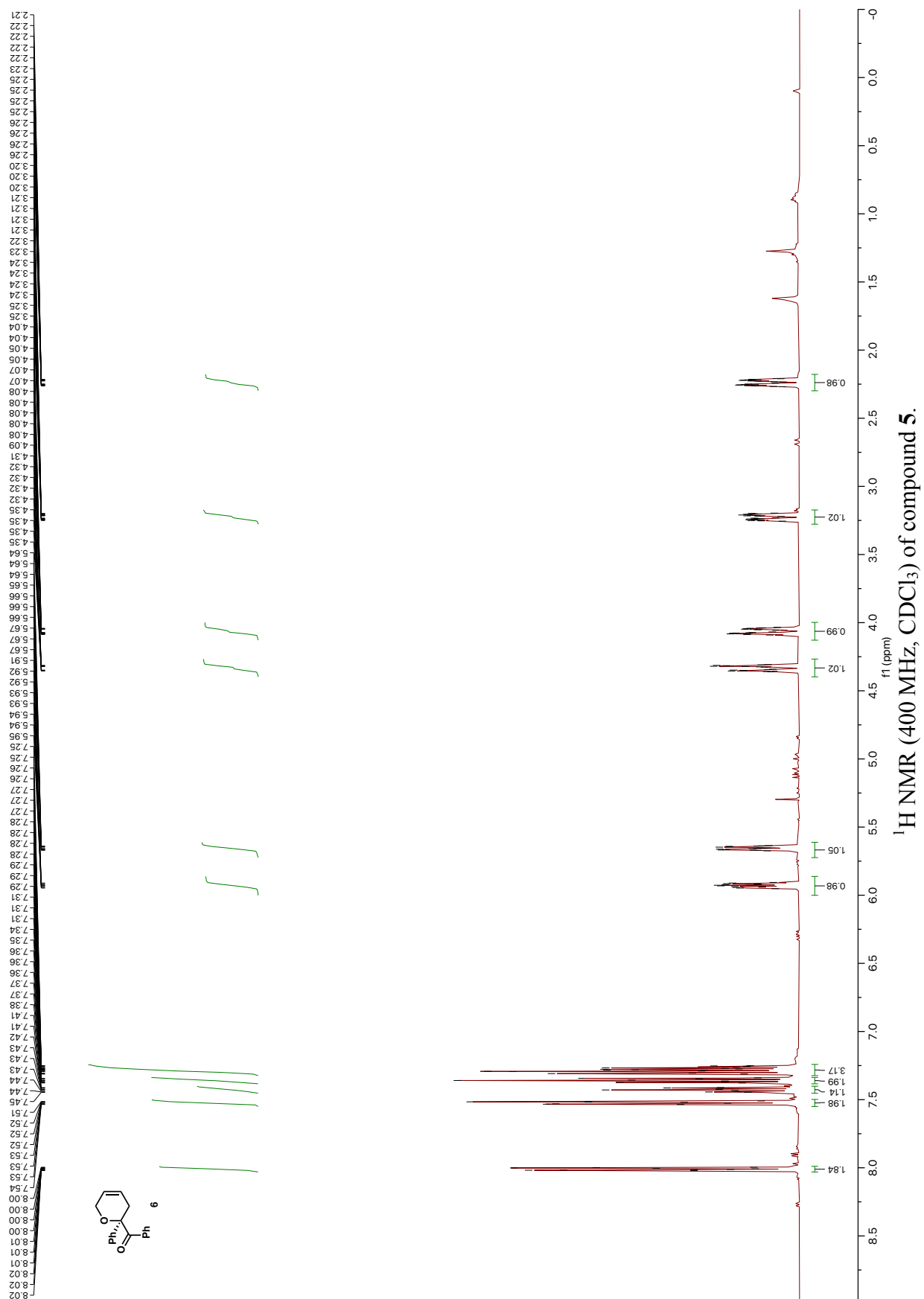


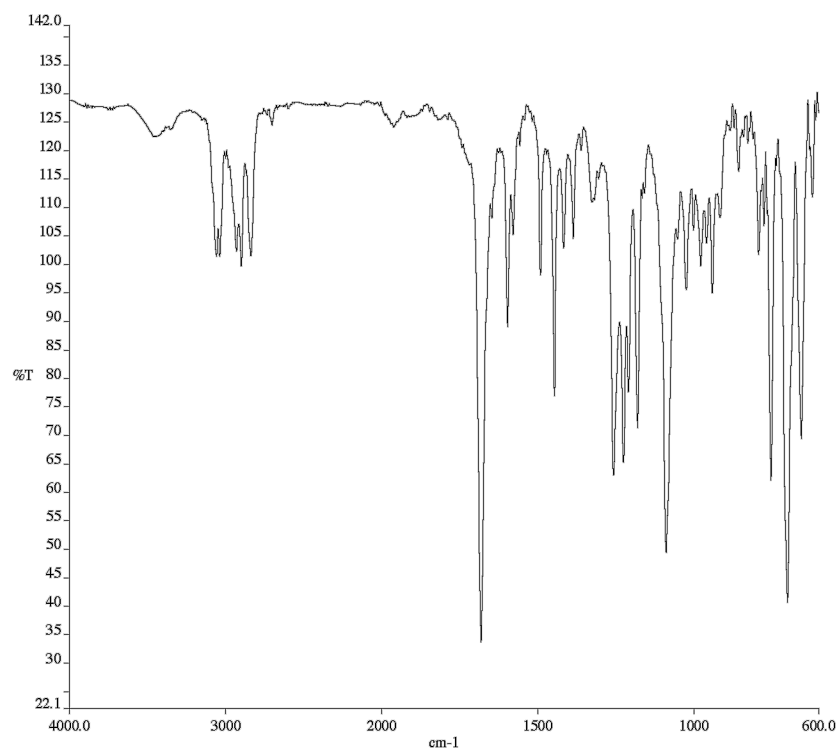
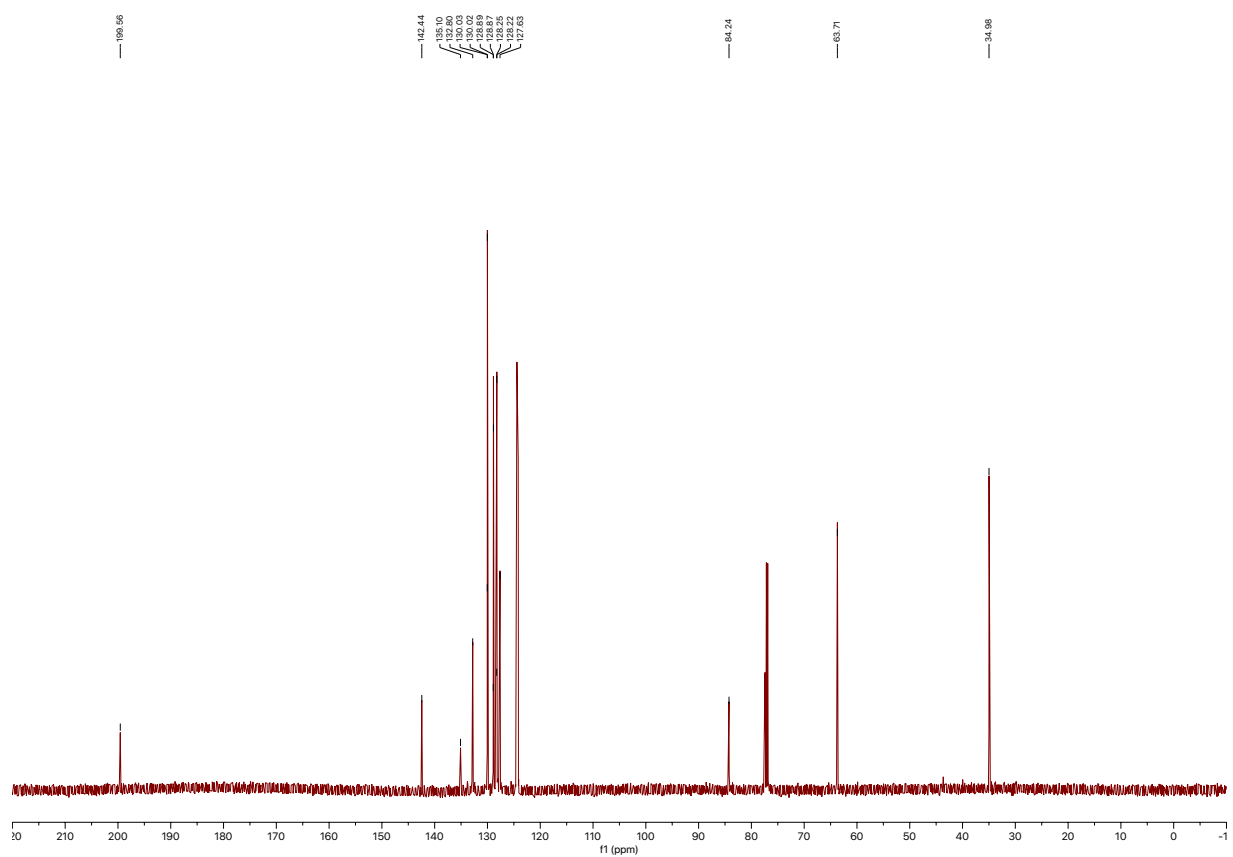
Infrared spectrum (Thin Film, NaCl) of compound 4.

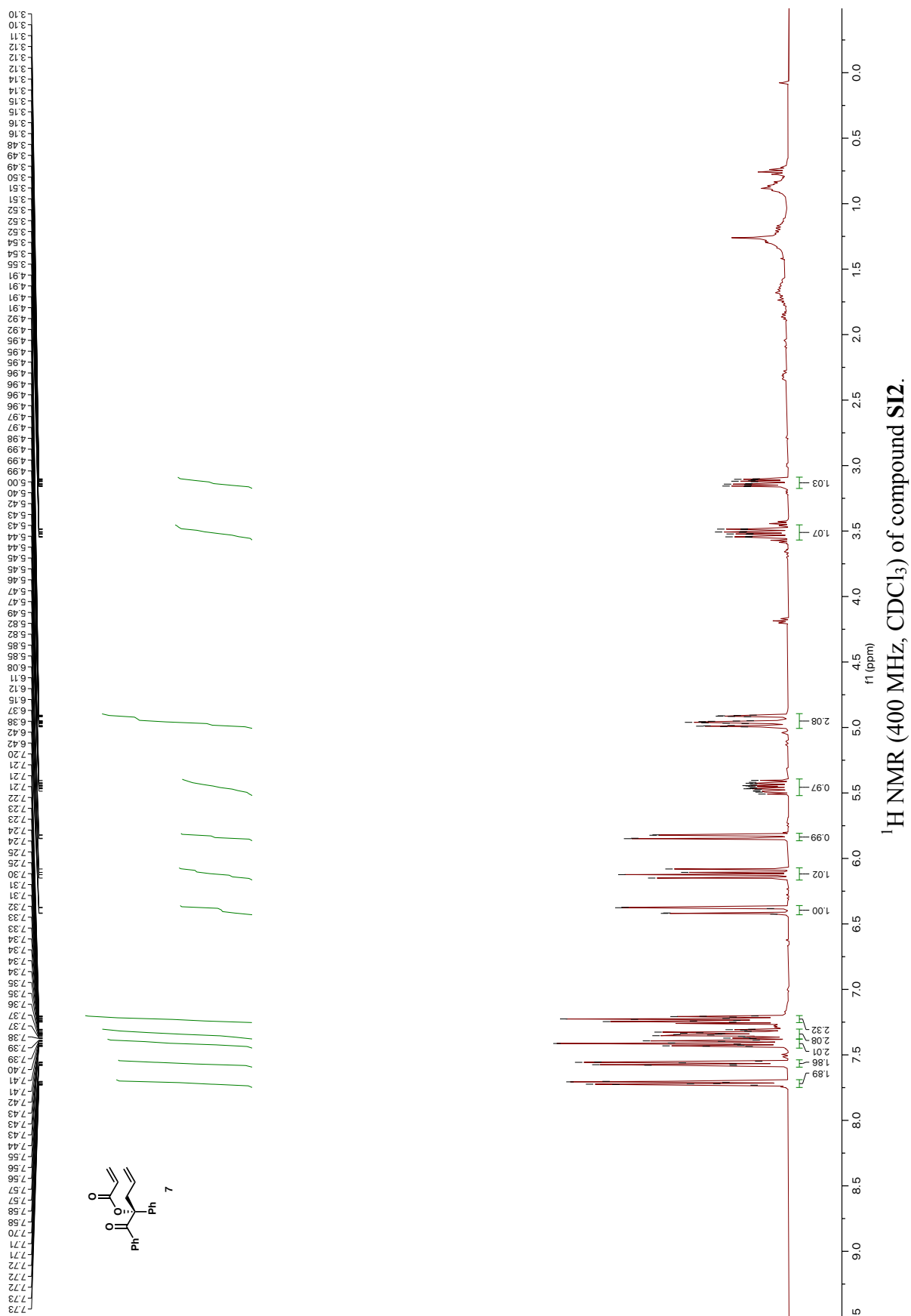
¹³C NMR (100 MHz, CDCl₃) of compound 4.

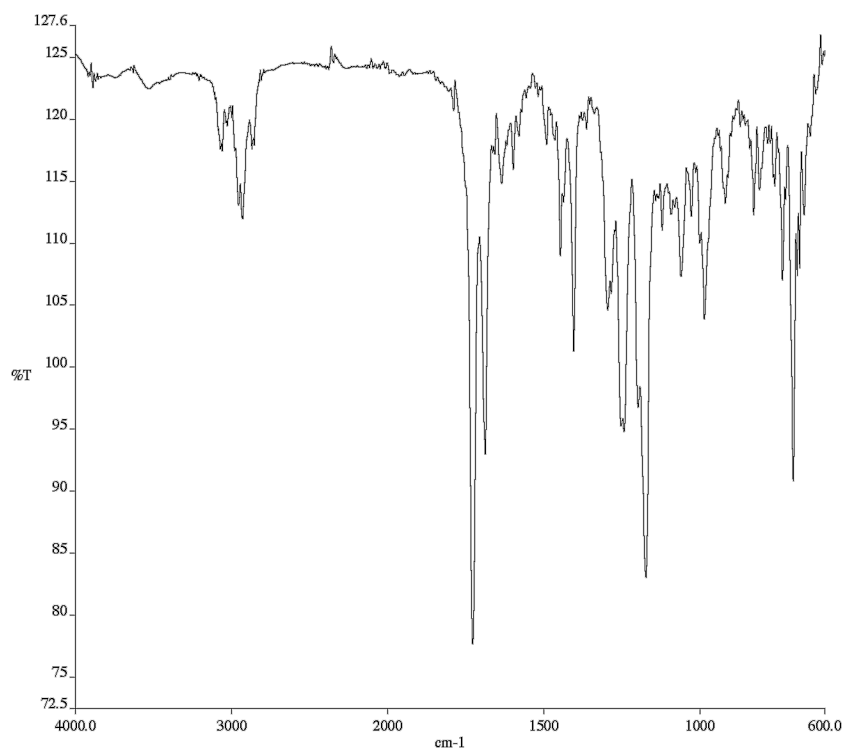
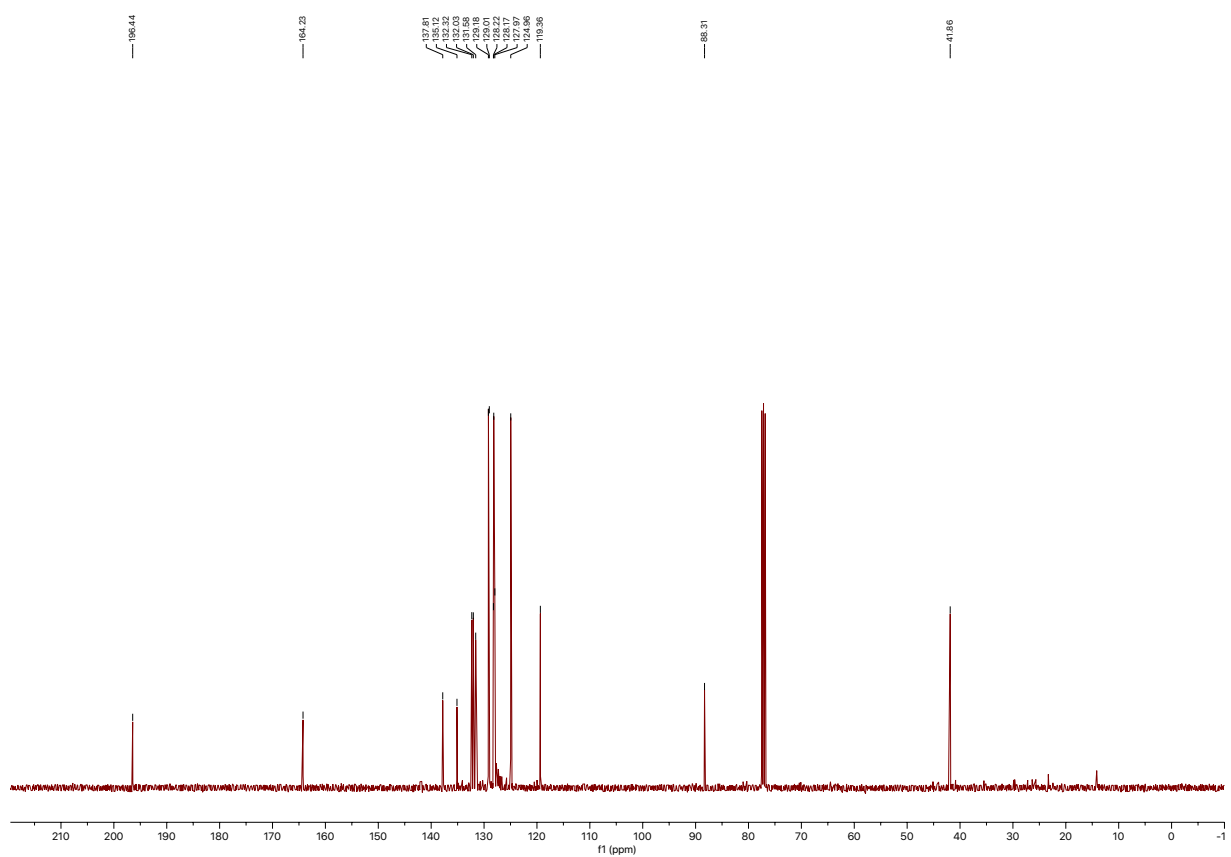


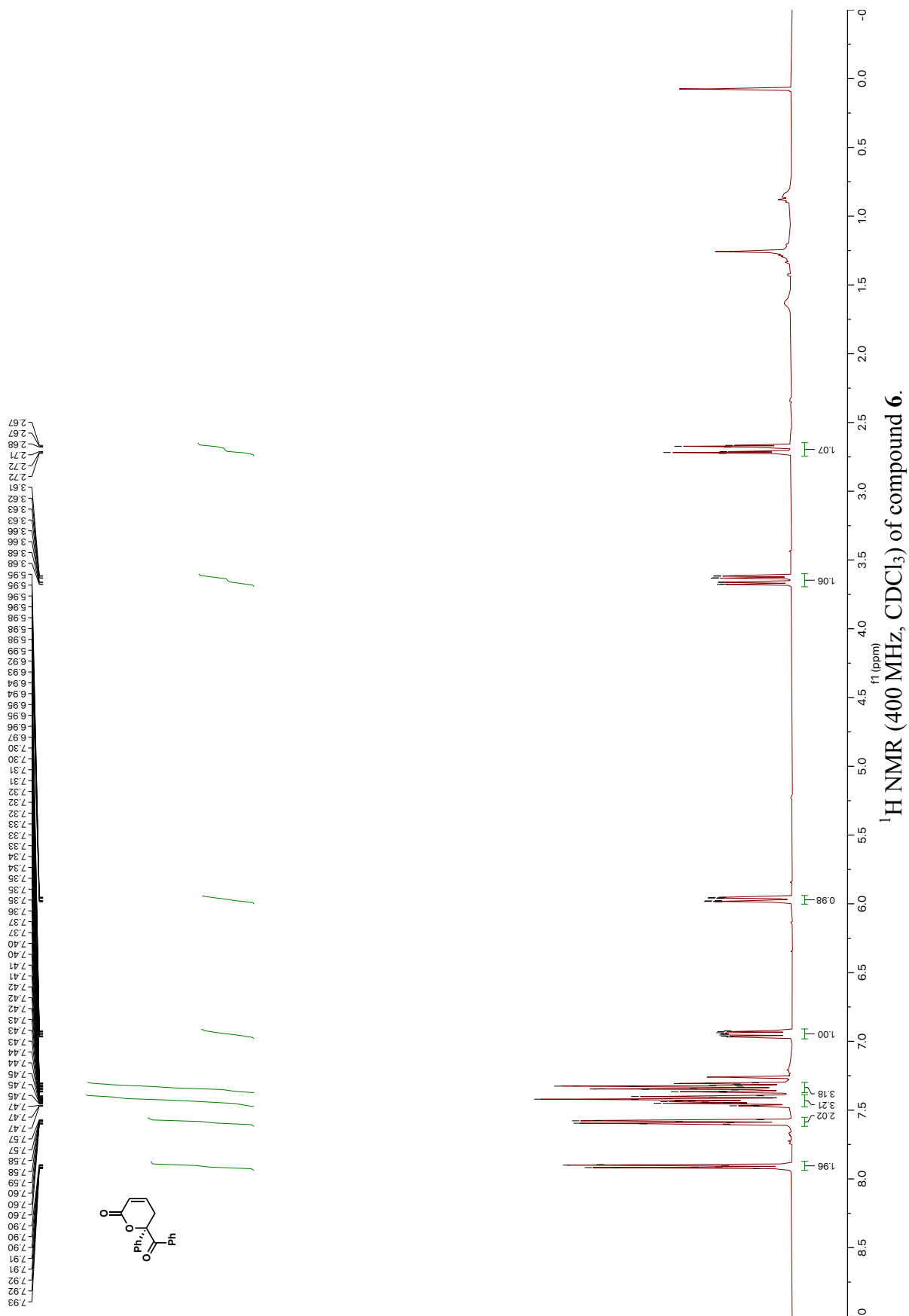
Infrared spectrum (Thin Film, NaCl) of compound **SII**.¹³C NMR (100 MHz, CDCl₃) of compound **SII**.

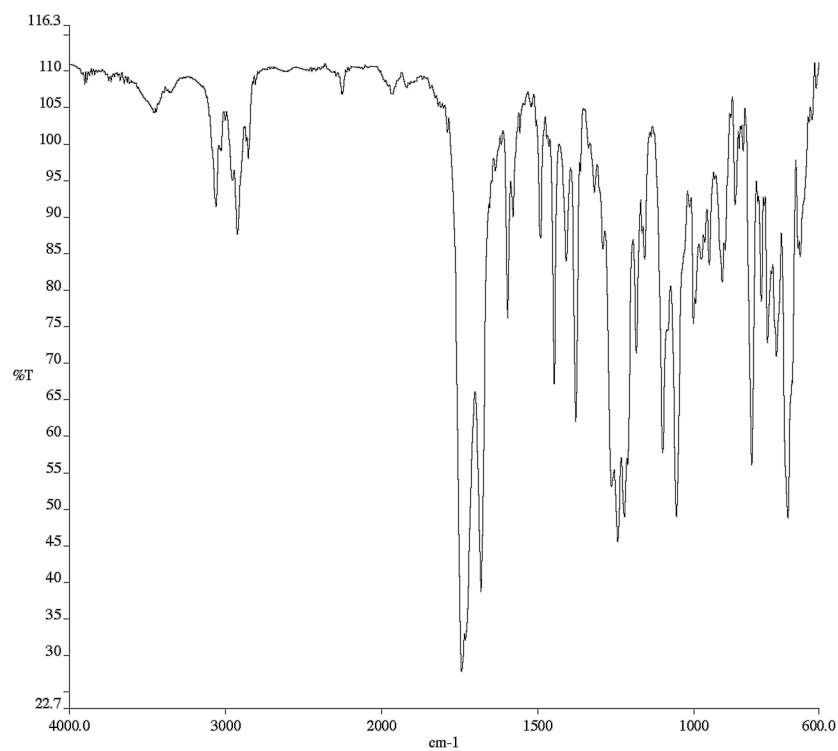


Infrared spectrum (Thin Film, NaCl) of compound **5**.¹³C NMR (100 MHz, CDCl₃) of compound **5**.

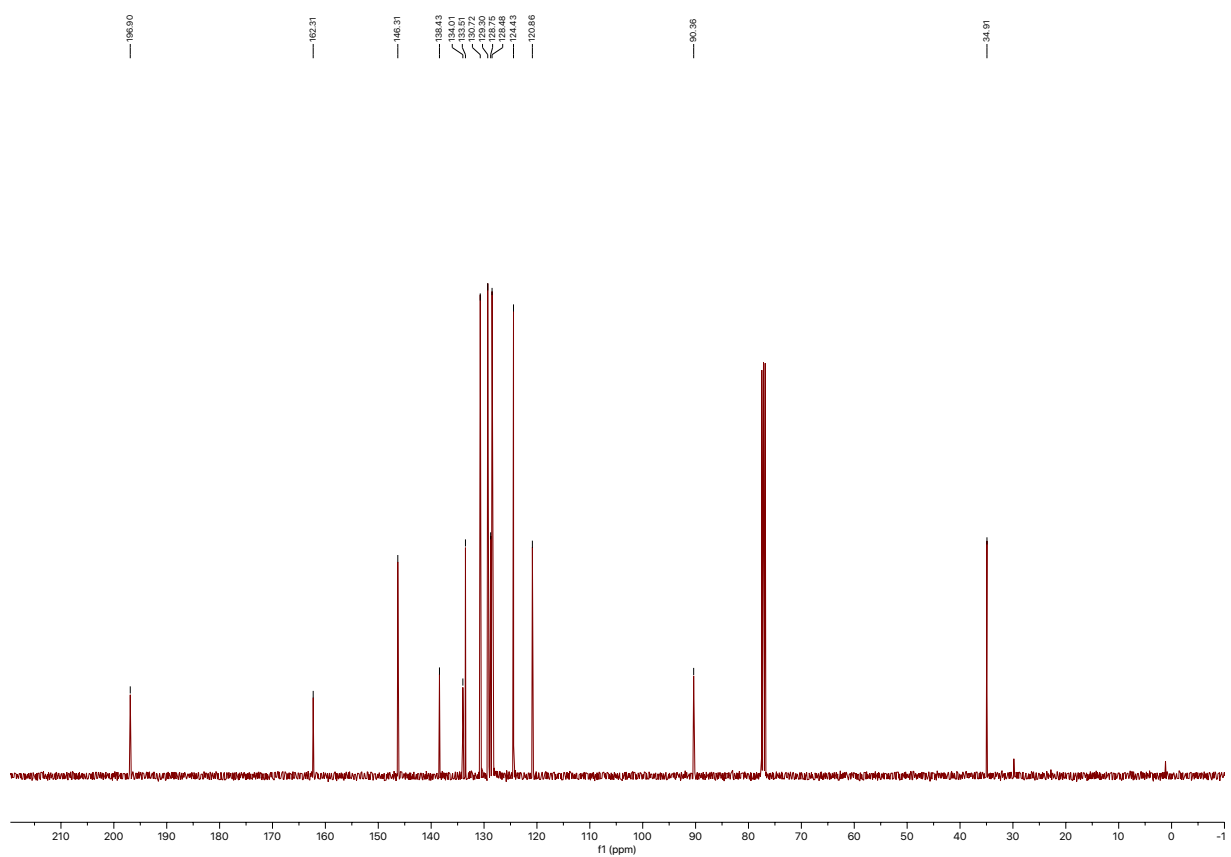


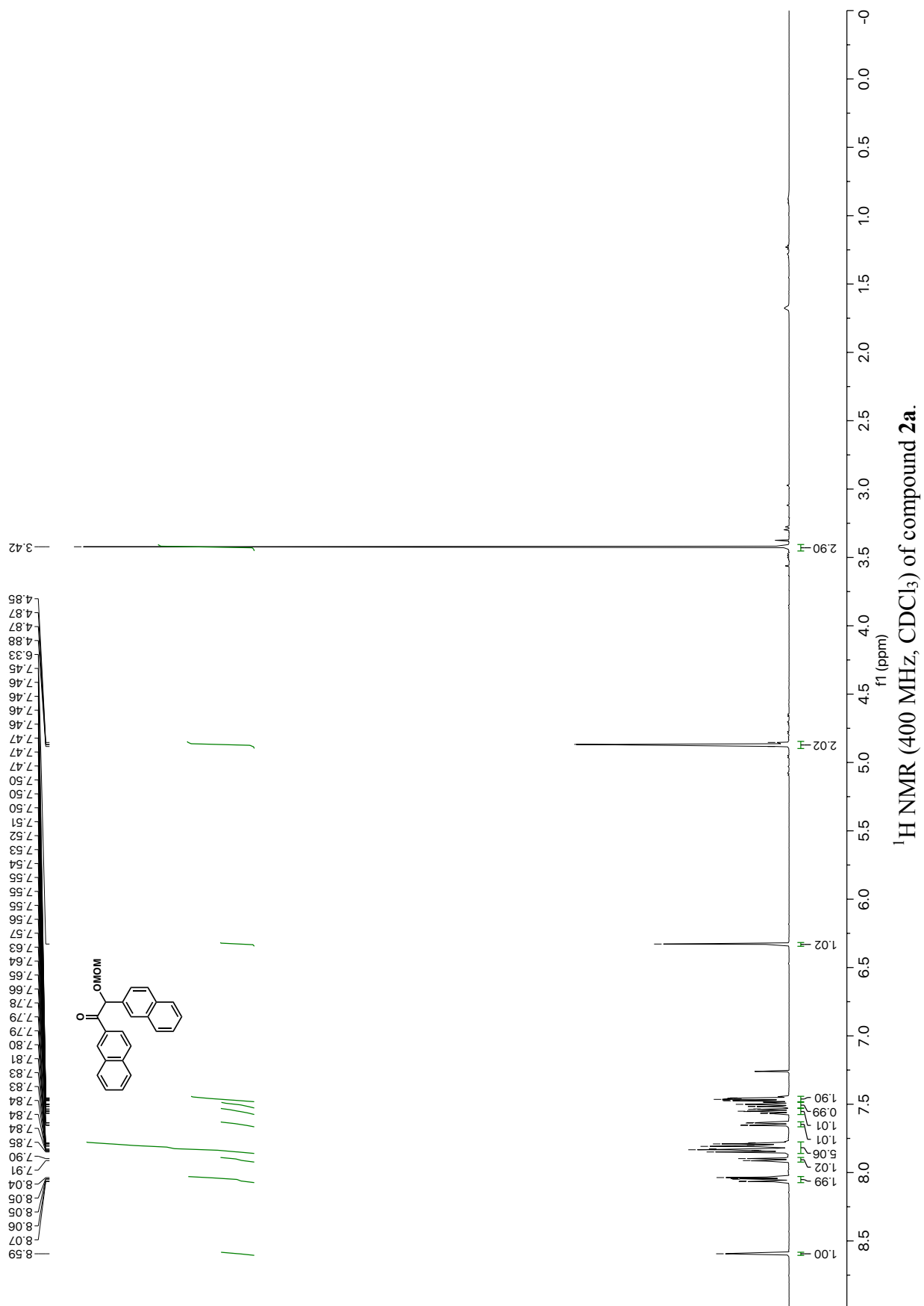
Infrared spectrum (Thin Film, NaCl) of compound **SI2**.¹³C NMR (100 MHz, CDCl₃) of compound **SI2**.

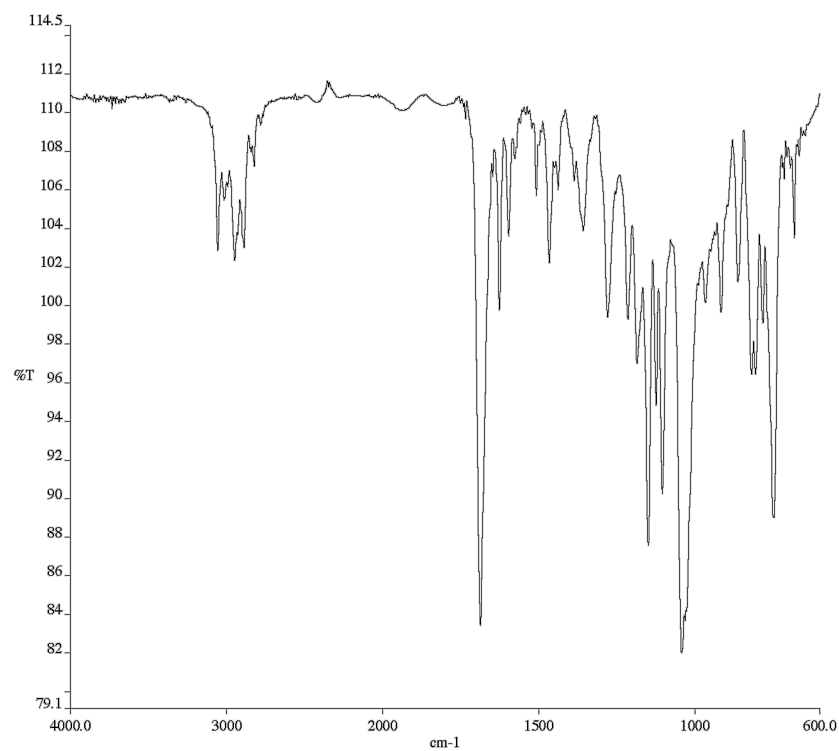
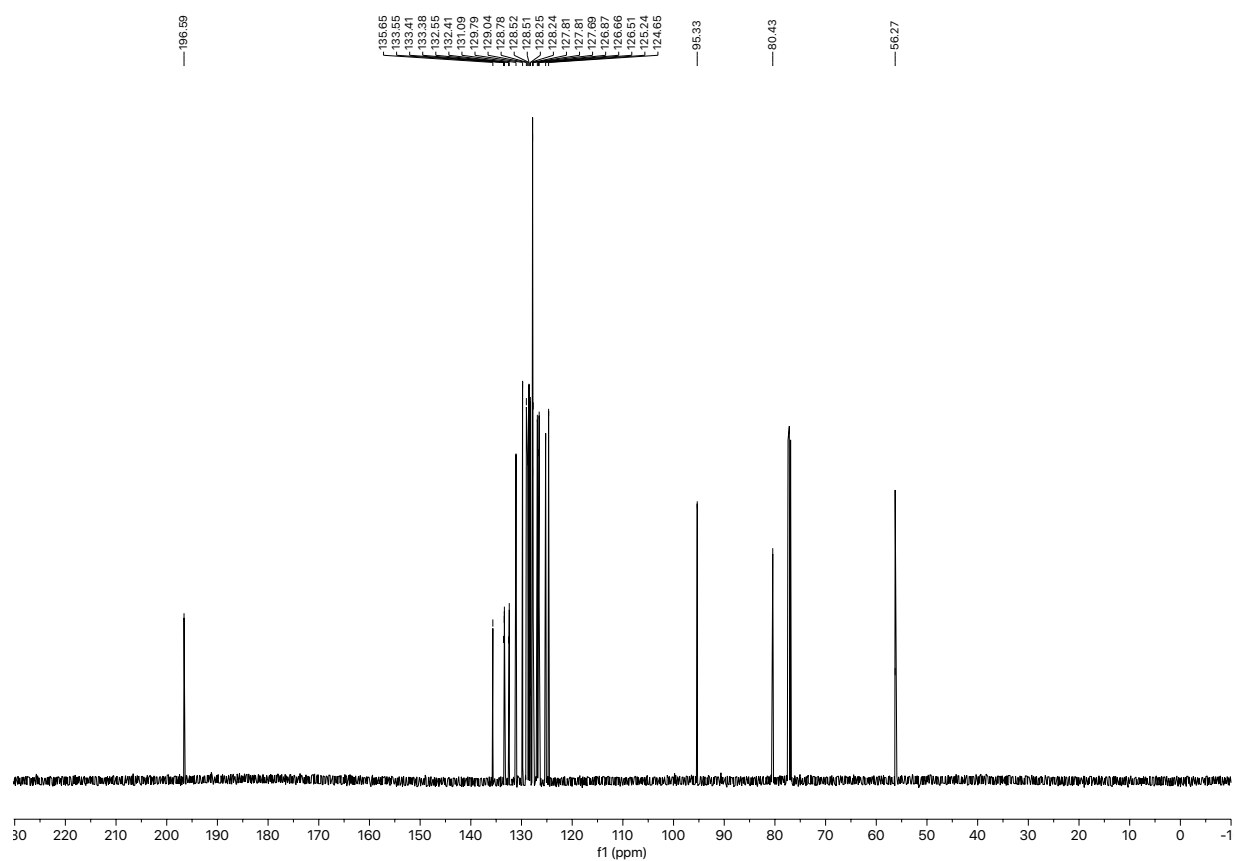


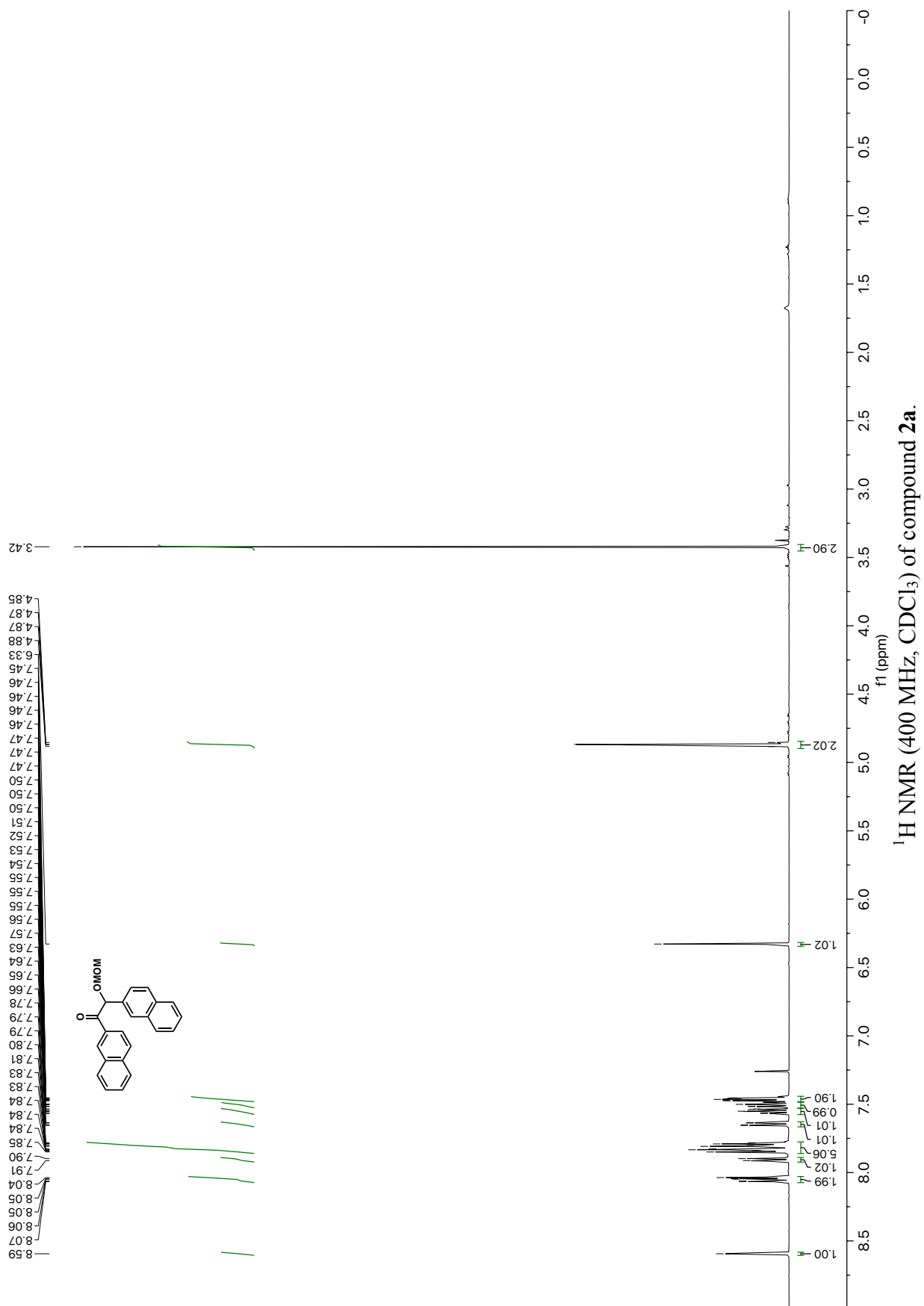


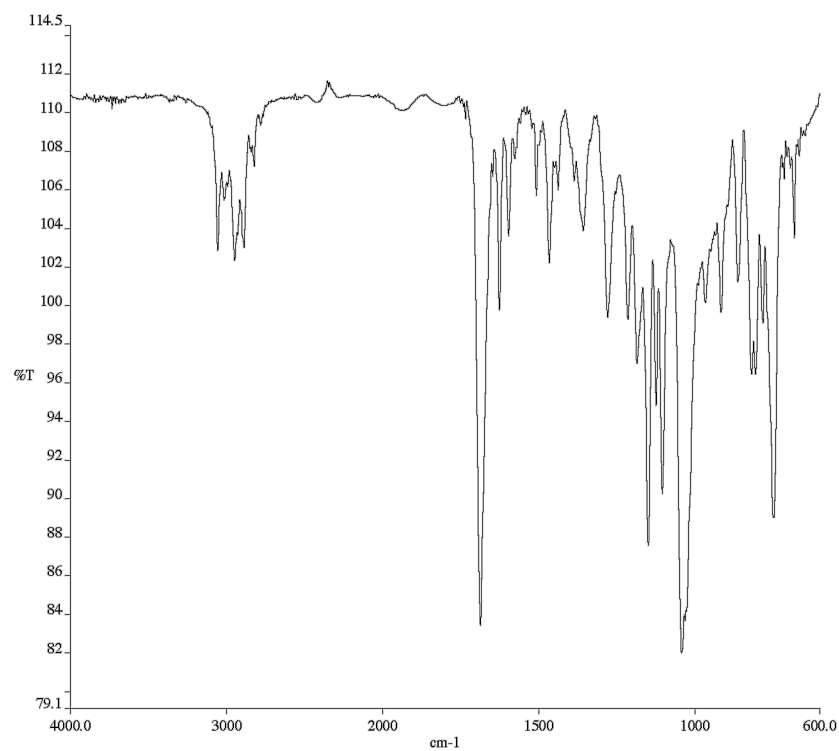
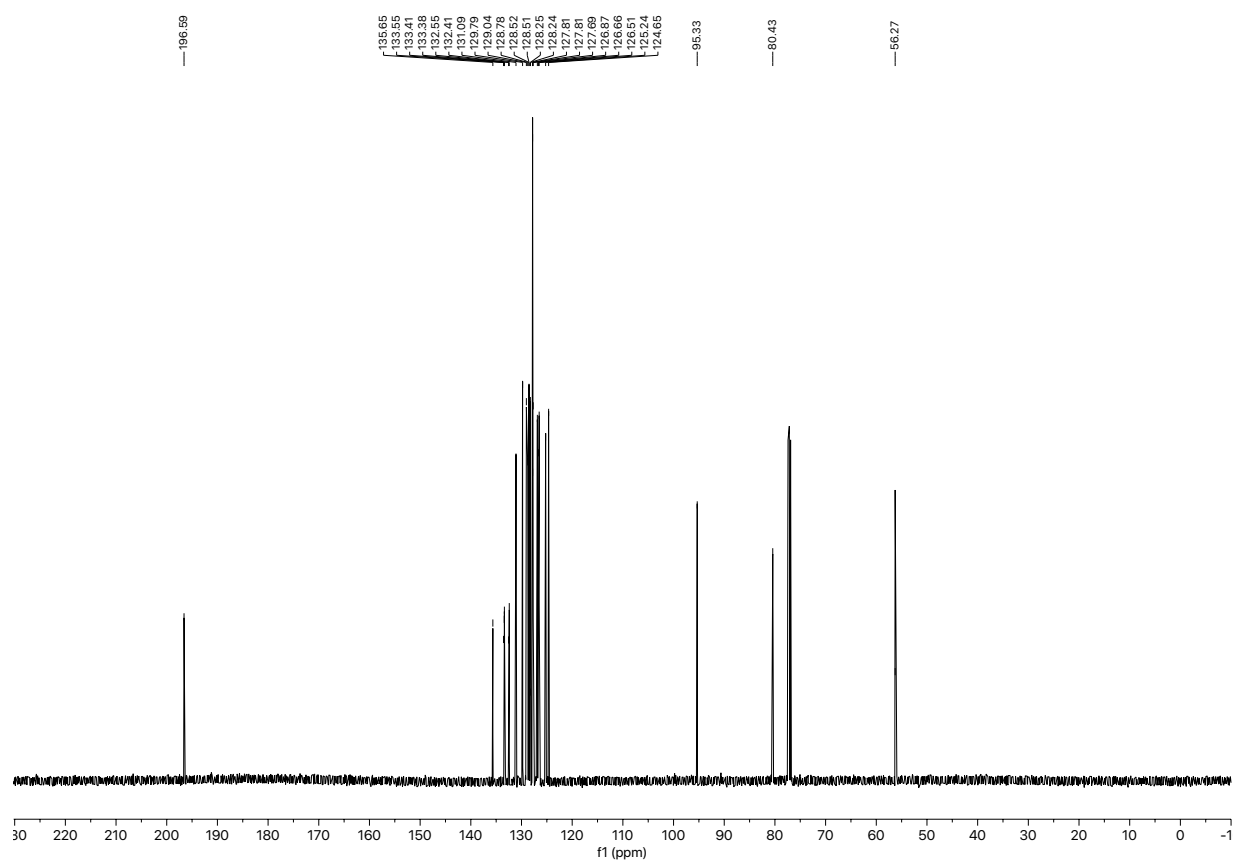
Infrared spectrum (Thin Film, NaCl) of compound 6.

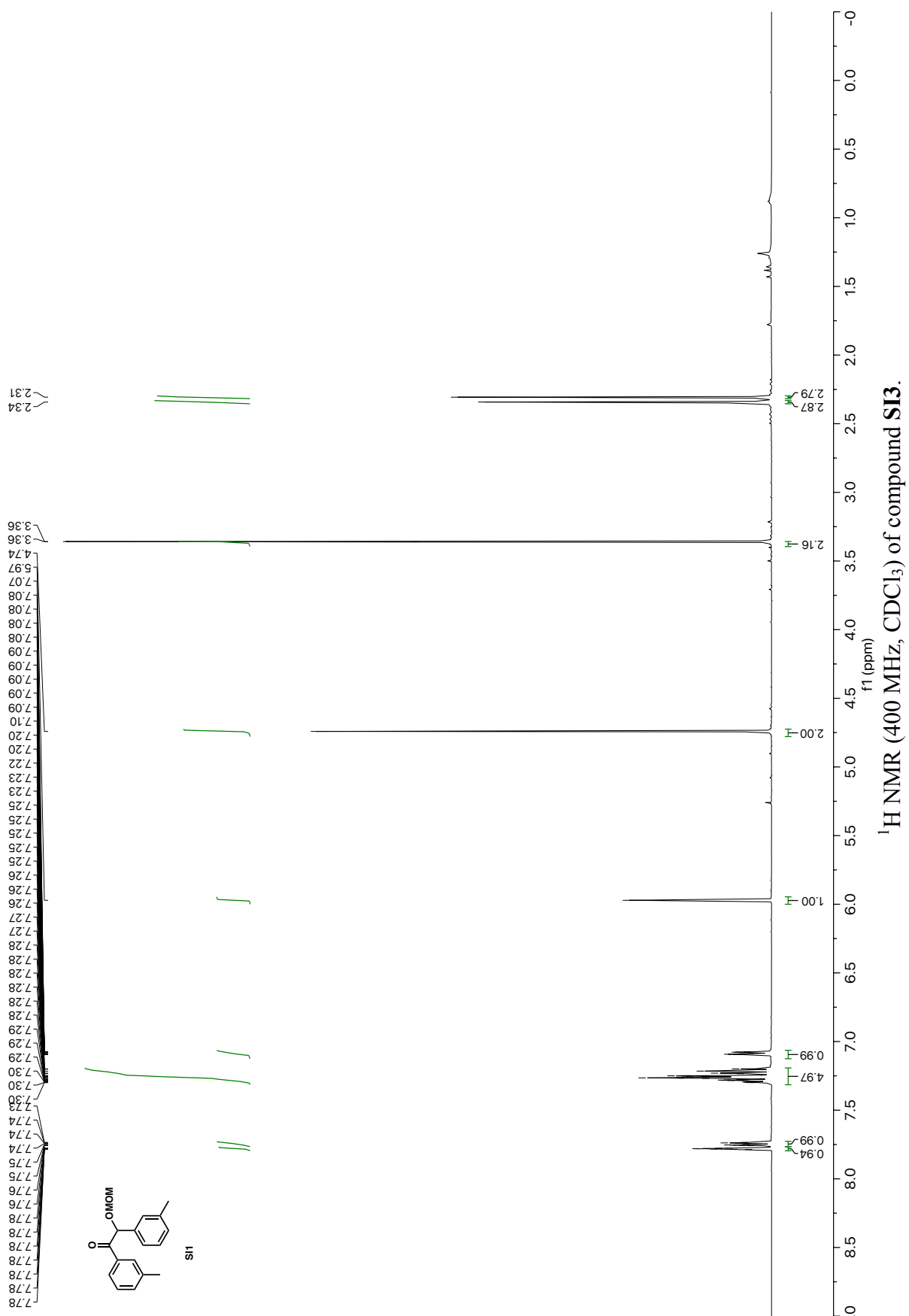
¹³C NMR (100 MHz, CDCl₃) of compound 6.

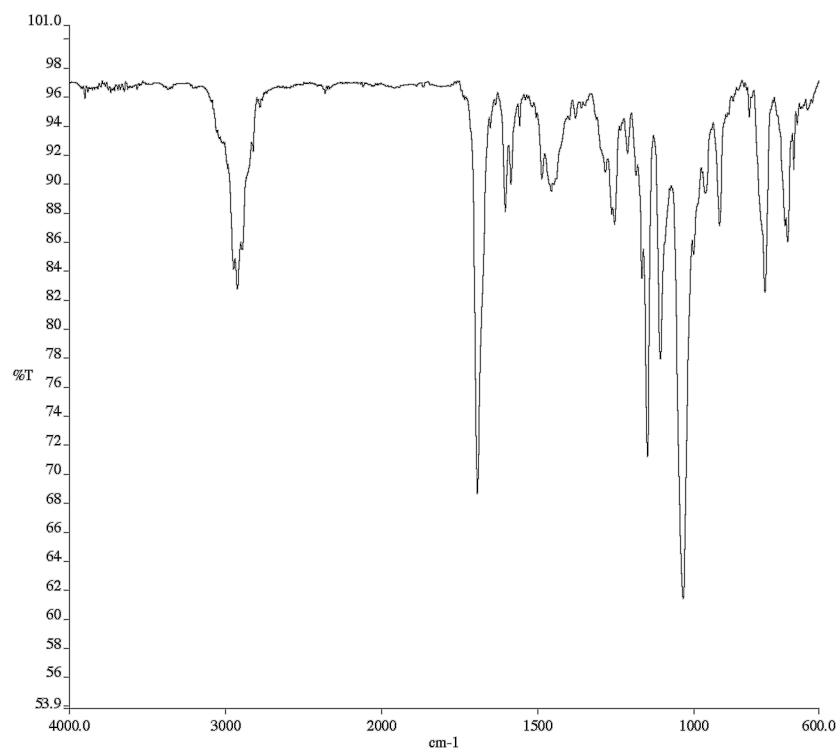
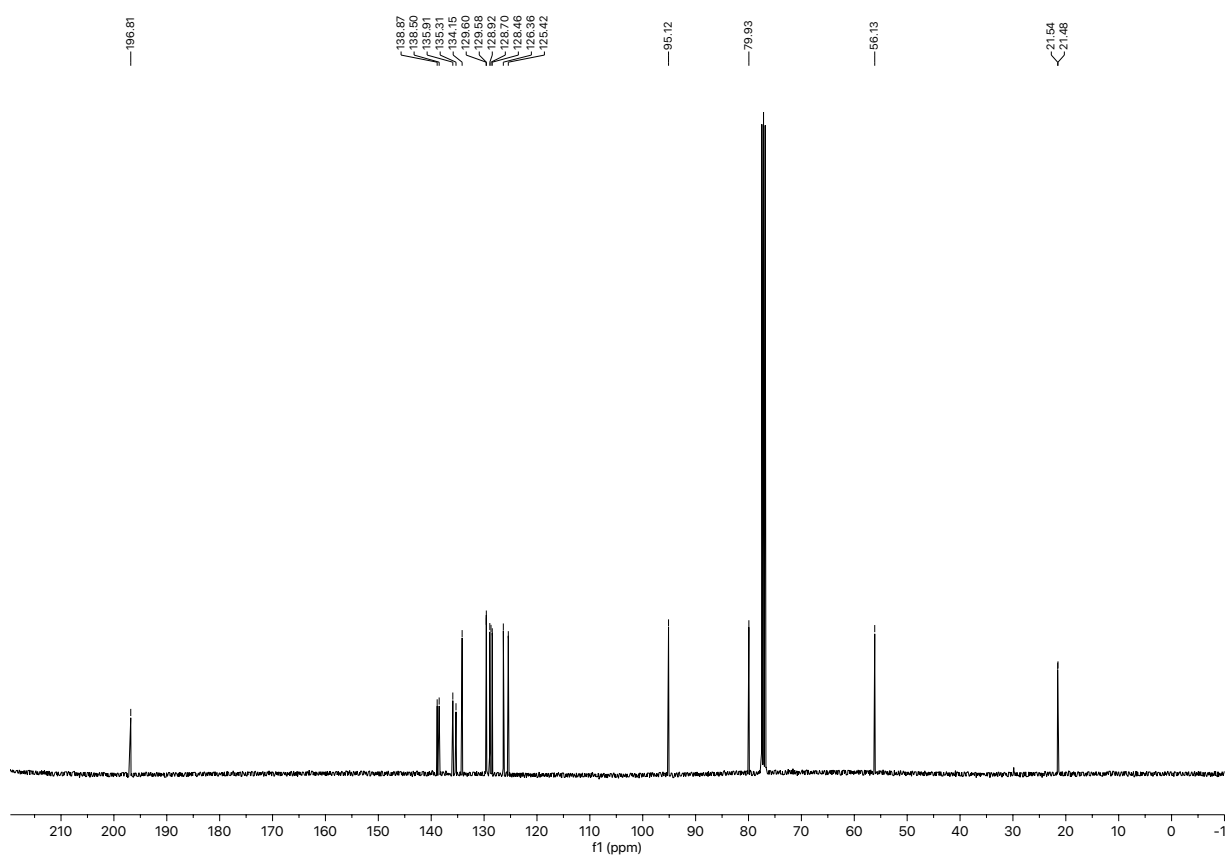


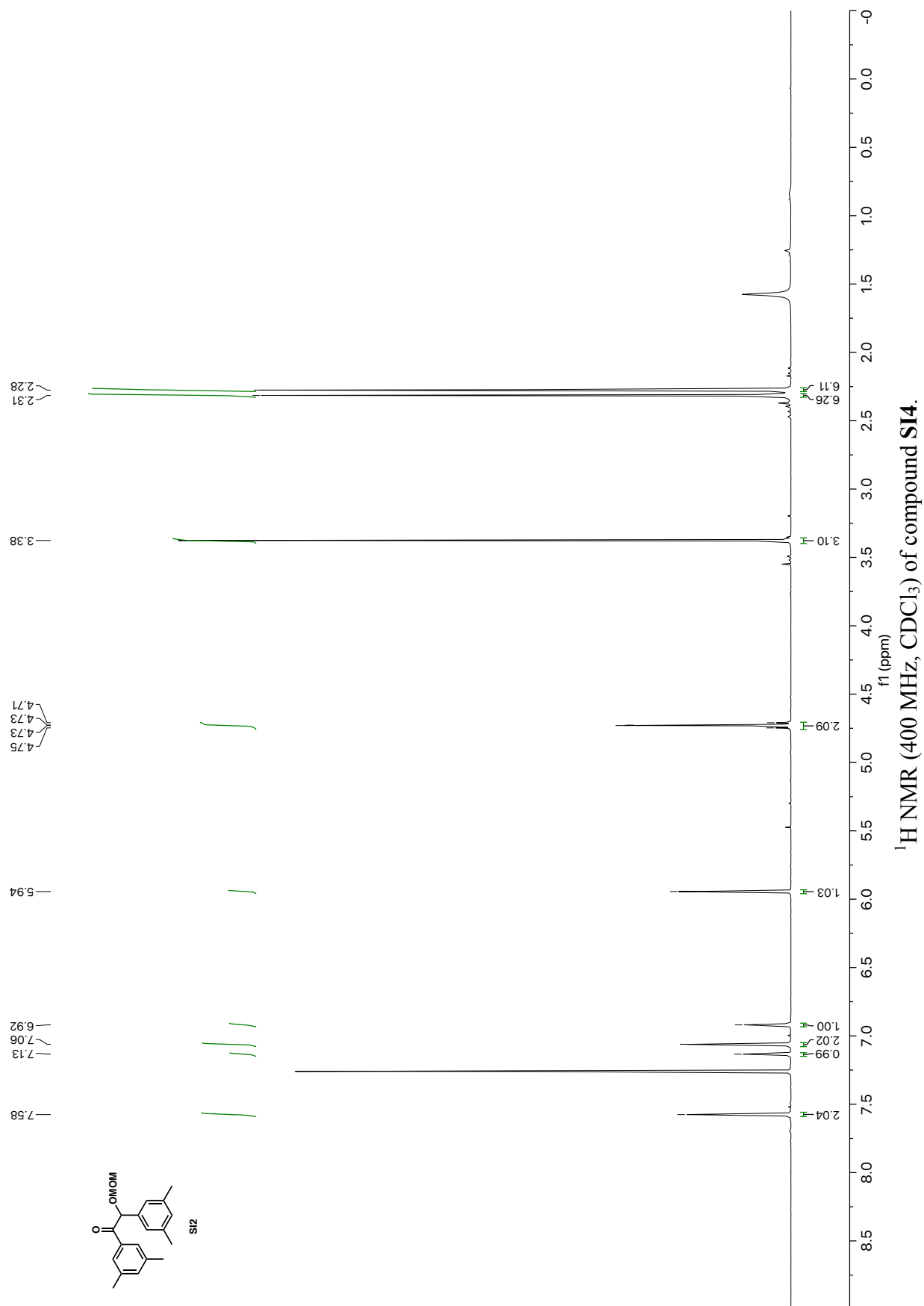
Infrared spectrum (Thin Film, NaCl) of compound **2a**. ^{13}C NMR (100 MHz, CDCl_3) of compound **2a**.

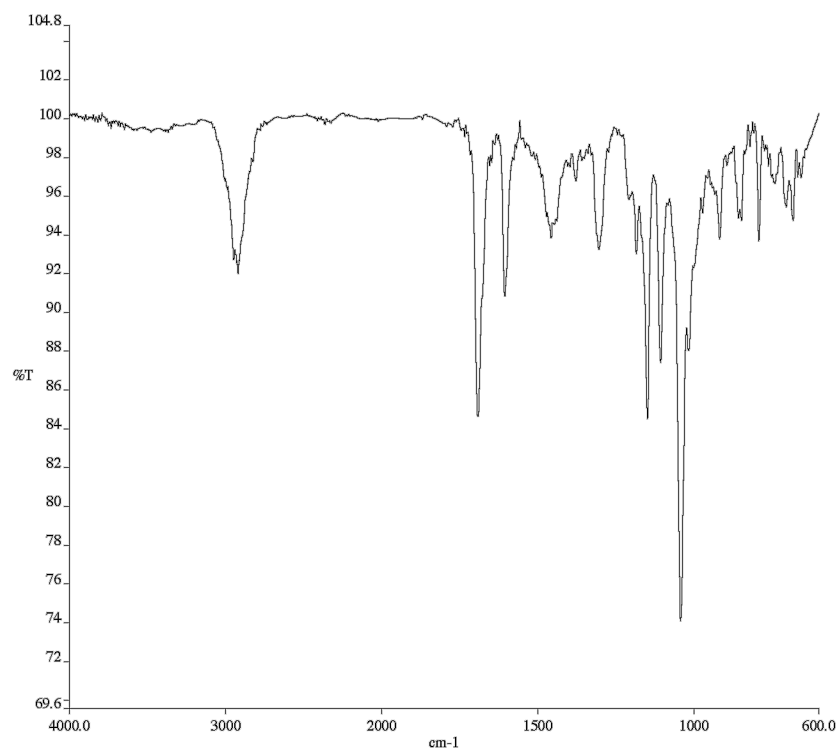
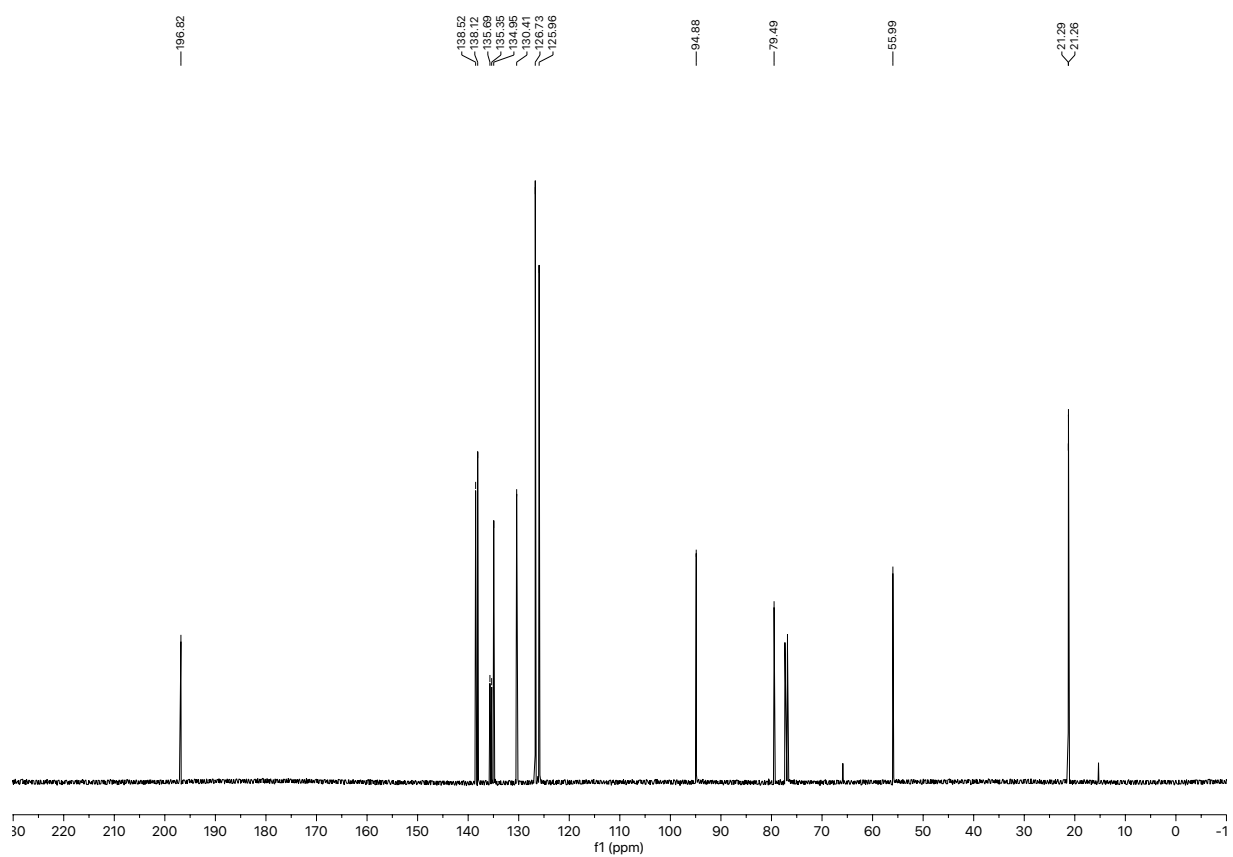


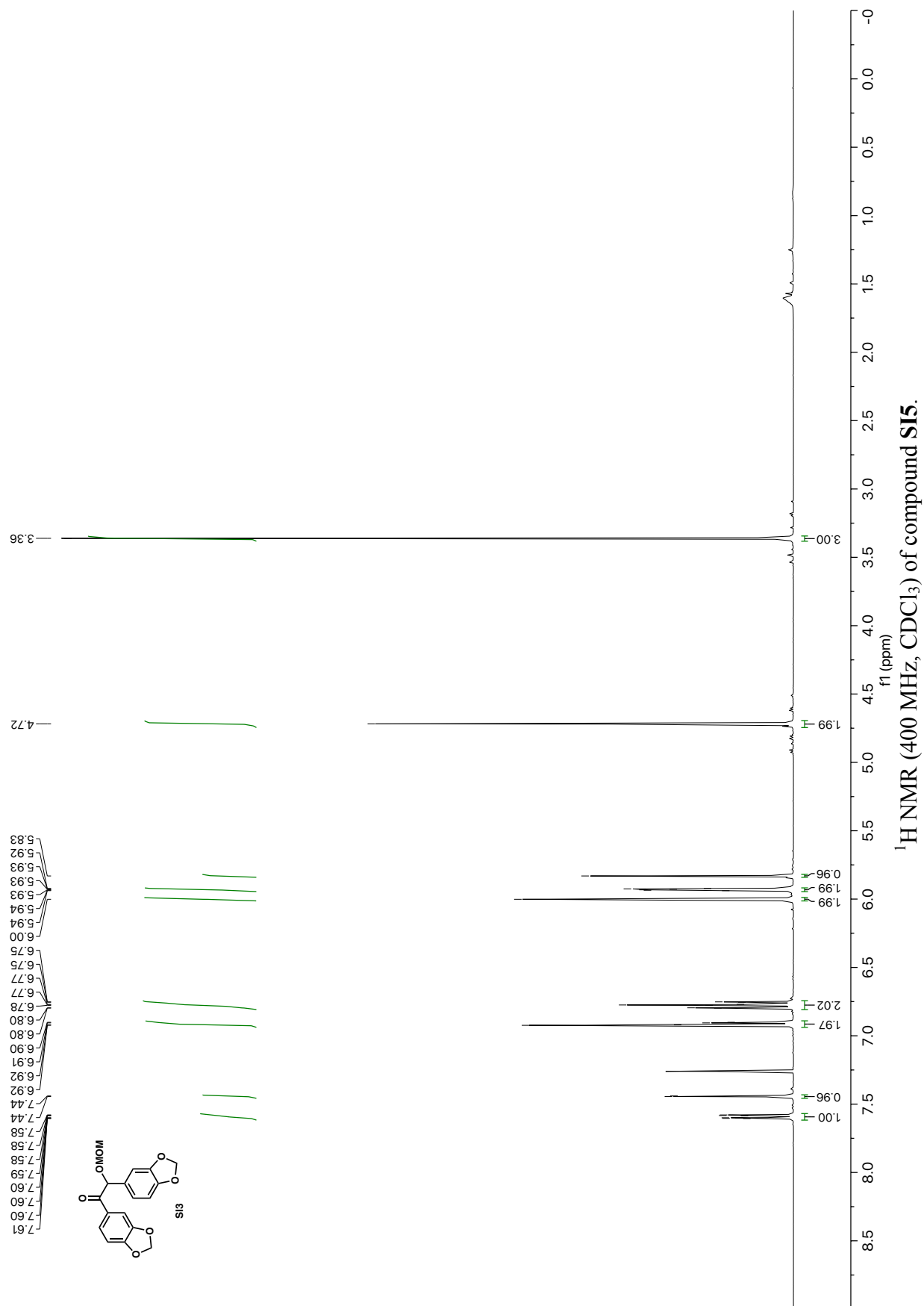
Infrared spectrum (Thin Film, NaCl) of compound **2a**.¹³C NMR (100 MHz, CDCl₃) of compound **2a**.

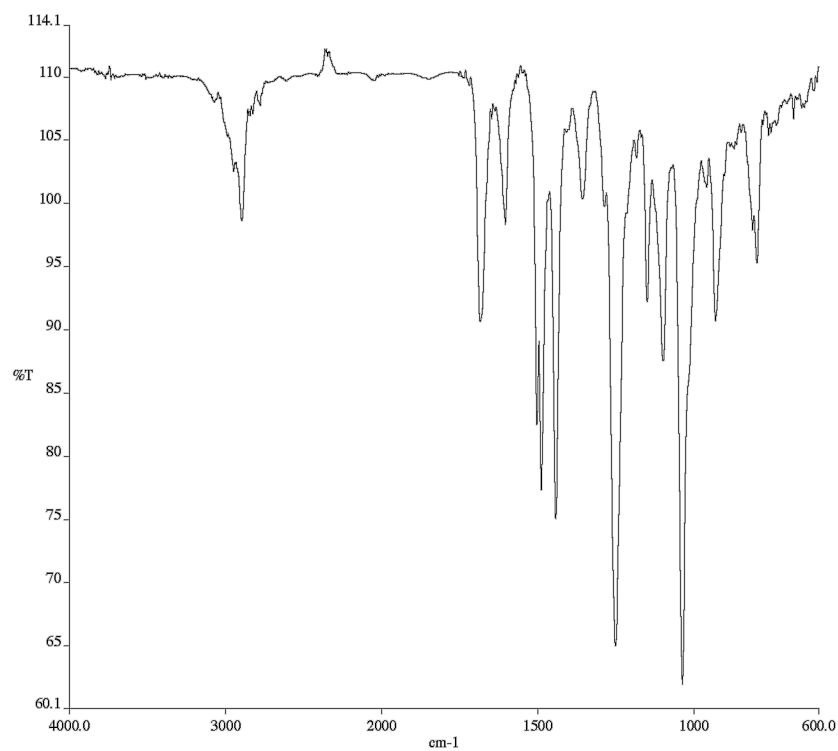
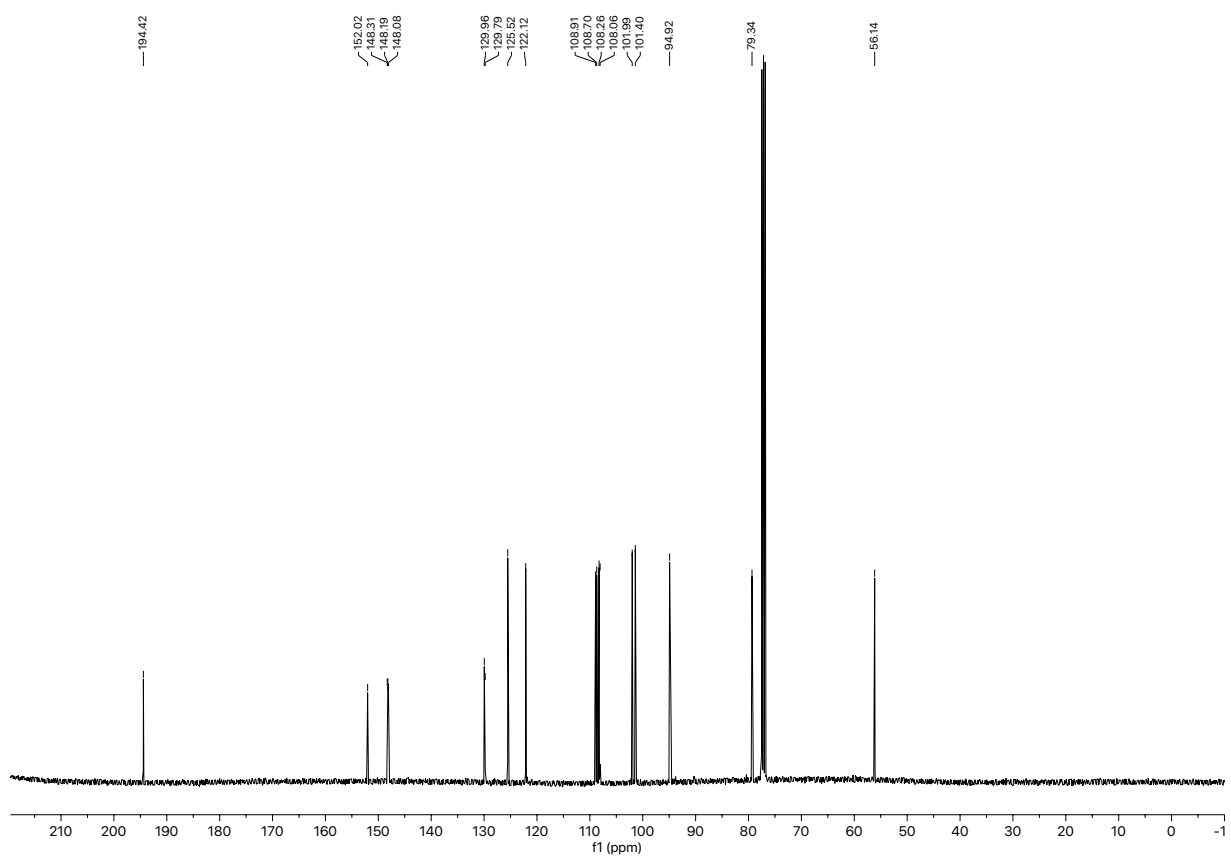


Infrared spectrum (Thin Film, NaCl) of compound **SI3**.¹³C NMR (100 MHz, CDCl₃) of compound **SI3**.



Infrared spectrum (Thin Film, NaCl) of compound **SI4**.¹³C NMR (100 MHz, CDCl₃) of compound **SI4**.



Infrared spectrum (Thin Film, NaCl) of compound **S15**.¹³C NMR (100 MHz, CDCl₃) of compound **S15**.